The Thermal Decomposition of an Unsaturated Polyester Resin

by

H.M. Mackinnon

SUMMARY

Unsaturated polyester resins are used in a large number of commercial products. They are formed by the copolymerisation of linear unsaturated polyester resins and unsaturated monomers; some of the unsaturated linkages in the polyester molecules copolymerise with the monomer to form a cross-linked resin.

This thesis describes some aspects of the thermal decomposition of poly(ethylene fumarate - methyl α-methylacrylate), a typical unsaturated polyester resin. Since Grassie ("The Chemistry of High Polymer Degradation Processes", Butterworths Scientific Publications, London, 1956) has made a comprehensive study of the pyrolysis of poly(methyl α-methylacrylate) itself, the work in this thesis deals mainly with poly(ethylene fumarate). To indicate the possible breakdown routes of this polyester, simple model compounds representing segments of the chain were first studied. These compounds were ethyl acrylate, ethylene diacrylate and methyl fumarate; their breakdown products and other simple compounds related to poly(ethylene fumarate) were separately pyrolysed.

The pyrolysis of poly(ethylene fumarate) itself was then studied. Three major competitive reactions were found:

(1) further linear polycondensation, followed by cross-linkage and eventual carbonisation,

(2) decarboxylation to a non-fumarate polyester,

and (3) alkyl-oxygen scission, yielding chain fragments which undergo further breakdown to low molecular weight compounds.

Thermal cross-linking of poly(ethylene fumarate) has previously been observed (Vincent, Ind. Eng. Chem., 1937, 29, 1267). Decarboxylation and alkyl-oxygen scission are predictable from the work on simple esters. The mechanism of decarboxylation is not known, but is suspected to be free radical. The reaction appears to result in the removal of every second carboxyl group from the polyfumarate chain. Alkyl-oxygen scission is a molecular reaction in which migration of the β-hydrogen atom yields acid and vinyl ester end-group fragments. In two other linear polyesters lacking an available β-hydrogen atom, alkyl oxygen scission was prevented and the polyesters were found in some respects to be more thermostable than poly(ethylene fumarate).

In pyrolysis of poly(ethylene fumarate-methyl α-methylacrylate) the initial reaction is liberation of monomeric methyl α-methylacrylate. This is thought to be a free radical chain reaction terminated at the inclusion of a polyester unit in the copolymer chain. The results of pyrolysis of other copolymers of methyl α-methylacrylate support this theory.

An apparatus was built for measuring the temperatures at which gaseous products of specific breakdown reactions are first detected. Under constant standard conditions, comparative values of these temperatures

were obtained for simple esters, poly(ethylene fumarate), poly(ethylene fumarate - methyl α-methylacrylate) and other related polyesters and copolymers of methyl α-methylacrylate. In poly(ethylene fumarate) decarboxylation was detected at a lower temperature than alkyl-oxygen scission, while in poly(ethylene fumarate - methyl α-methylacrylate) monomeric methyl α-methylacrylate is liberated before any products derived from breakdown of the polyester chain.

It is suggested that this monomer liberation might be suppressed by dispersion of a suitable free radical inhibitor in the resin. Decarboxylation of the polyester chain, if it is a free radical reaction, might similarly be suppressed. The only apparent method of eliminating alkyl-oxygen scission is by modifying the structure of the polyester to exclude the available β-hydrogen atom.

THE PYROLYSIS OF AN UNSATURATED CROSS-LINKED POLYESTER RESIN

by

H. M. MacKinnon

A Thesis submitted in accordance with the regulations governing the award of the Degree of Doctor of Philosophy in the Faculty of Science of the University of Glasgow.

Preface

This thesis describes a research project carried out under the direction of Professor P.D.Ritchie, B.Sc., Ph.D., F.R.I.C., F.P.I., F.R.S.E., in the Department of Chemical Technology, the Royal College of Science and Technology, Glasgow.

I thank Professor Ritchie for his unfailing help and guidance throughout the course of the work. For their assistance in many ways I thank also my colleagues and members of the Department staff.

Part of the work described has been published in the Journal of the Chemical Society ("Studies in Pyrolysis. Part XI. Competitive Routes in the Pyrolysis of Esters: Phenyl Acrylate and Phenyl α-Methylacrylate." H.M.Mackinnon and P.D.Ritchie, June, 1957, (498), pages 2564-2569).

H.M.Mackinnon

The Royal College of Science and Technology,
September, 1958.

Synopsis

Poly(ethylene fumarate - methyl α-methylacrylate) was selected as a typical unsaturated cross-linked resin. The initial thermal degradation in this resin is liberation of monomeric methyl α-methylacrylate. Breakdown of the cross-linking poly(ethylene fumarate) chain requires a higher temperature, the major reactions being decarboxylation and alkyl-oxygen scission.

The pyrolyses of a number of model compounds representing segments of the resin structure are discussed. A new type of apparatus for determining the onset temperatures of specific breakdown reactions under constant conditions is described.

Suggestions are made whereby the thermal stability of the resin might be improved by modifications of its composition and structure.

: C O N T E N T S :

LIST OF FIGURES

§§§§§§§§§§

1. INTRODUCTION

Unsaturated polyester resins, of which poly(ethylene fumarate - methyl α-methylacrylate) (I) is an example, have in recent years achieved considerable commercial importance. Such resins consist essentially of an unsaturated linear polyester copolymerised with an unsaturated monomer to yield a cross-linked product as illustrated in Figure 1. Poly (ethylene fumarate) (II) is the most commonly used polyester; it was apparently first prepared in 1894 by Vorlander[1], who recorded that it formed a hard, insoluble material on heating Considerable time elapsed before this property was made use of in manufacture of cross-linked resins. Patents granted in 1936[2] describe resins prepared by copolymerisation of II and unsaturated hydrocarbons such as divinyl acetylene and cuprene. In 1937, Vincent[3] studied the cross-linking of II itself, showing the reaction to be catalysed by light, heat or oxygen traces, and in 1940 Ellis[4] employed benzoyl peroxide catalyst in cross-linking. The first example of the modern type of resin was reported in 1940 by Rust[5], who copolymerised II with styrene, vinyl acetate and methyl α-methylacrylate. Styrene is now the most commonly used comonomer; others include vinyl acetate, methyl α-methyl-acrylate, vinylidene chloride, diallyl phthalate and triallyl cyanurate.

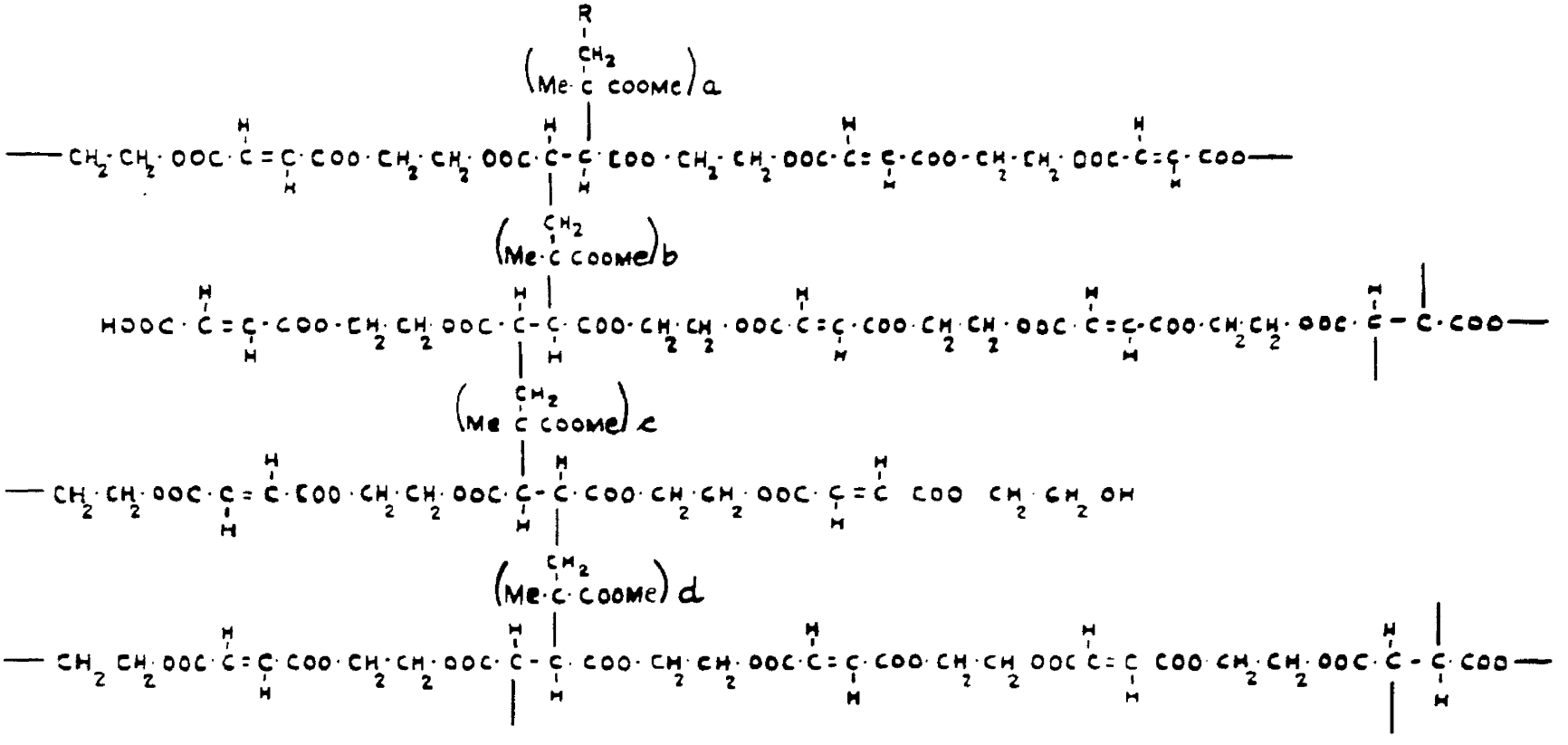


FIG. 1 - REPRESENTATION OF POLY (ETHYLENE FUMARATE - METHYL METHACRYLATE) STRUCTURE.

R, CATALYST RESIDUE; a, b, c, d, ETC, ca. 18 FOR EQUIMOLAR METHACRYLATE AND FUMARATE FEED RATIO.

A solution of II in the comonomer is rapidly and easily cured in a low-pressure mould, and for this reason the materials are known as "contact resins". As paper, cloth or glass-fibre supported laminates, they form strong, light-weight, corrosion-resisting materials widely used in such products as decorative table-tops, car, bus and boat bodies, electrical insulators and sports equipment. Their transparency to radar is utilised in aircraft and military installations.

Compared to metals, resin laminates are at a disadvantage in that they have a much lower maximum working temperature. It has been estimated[6] that at 300° an organic polyester could only be used for a very limited time. The eventual aim of the present study was to raise the working temperature, by elucidating the manner of thermal breakdown and thereby indicate means of preventing or reducing degradation.

Several reasons influenced the choice of I as representative of contact resins. Firstly, the extensive study of the thermal degradation of poly(methyl α-methylacrylate) by Grassie[7] allowed investigations to be concentrated initially upon breakdown in the cross-linking polyester chain. Secondly, II is completely soluble in methyl α-methylacrylate while in styrene, for example, it is not and the system is complicated by the necessary addition of a third monomer or solvent. This second reason was of equal importance in the

kinetic study of the hardening reaction of contact resins undertaken concurrently in these laboratories[8,9].

Commercial contact resins normally incorporate saturated dibasic acid units in the polyester chain to space out the cross-linking double bonds and increase the resin flexibility Although the effect of these saturated units is considered, the present work is concerned mainly with a simple fumarate - methacrylate system in which breakdown may occur in one of three sites:

(1) in the polyfumarate chain,

(2) in the α-methylacrylate chain,

or (3) at points of cross-linkage.

Initial investigations on the breakdown of II, representing residual unsaturated polyfumarate units in the chain, showed degradation to be very complex. It was therefore necessary to pyrolyse simple model compounds representing segments of II to indicate the probable polyester breakdown routes. Further breakdown of model compound primary pyrolysis products was elucidated by separate pyrolysis of these products, and a number of related compounds pyrolysed to confirm postulated breakdown routes. The information thus gained was then applied in the investigation of the pyrolysis of II itself.

Breakdown in the α-methylacrylate chain and at points

of cross-linkage was also elucidated with the help of information derived from the study of model and related compounds. In this section of the work, considerable assistance was obtained from Grassie's previous investigations.

Most of the information on breakdown of I was derived from a qualitative and, as far as possible, quantitative study of competitive breakdown routes, estimated by analysis of pyrolysis products. Compounds investigated in this manner are listed in Table 1 (pp.5 and 6), where the relationship of each pyrolysand to I is indicated. Supplementary information was obtained by a study of the onset or threshold temperatures, under constant conditions, of specific breakdown routes; compounds thus investigated are listed in Table 2 (p.7). From the combined results it is possible to deduce a fairly comprehensive picture of the breakdown of I, and to suggest structural modifications to improve the thermal stability of the resin.

Before discussion of the results, a brief review of relevant literature is included.

1.1. The Pyrolysis of Simple Esters.

Although frequent early examples in the literature quote one exclusive route in ester breakdown, it is now known that almost all esters break down by two or more primary competiti

Table 1- Pyrolysands studied qualitatively and semi-quantitatively.

	Pyrolysand	Structure	Relationship to I
I,	Poly(ethylene fumarate - methyl α-methylacrylate)	See Figure 1	
II,	Poly(ethylene fumarate)	-COO.CH:CH.COO.CH_2.CH_2- (trans)	Polyester chain
III,	Poly(methyl α-methylacrylate)	-CH_2.C.Me- COO.Me	α-Methylacrylate chain
IV,	Ethyl acrylate	CH_2:CH.COO.CH_2.CH_3	Model for II
V,	Acrylic acid	CH_2:CH.COOH	Product of II, IV and XII
VI,	Acraldehyde	CH_2:CH.CHO	Product of IV
VII,	Ethanol	CH_3.CH_2OH	Product of IV
VIII,	Phenyl acrylate	CH_2:CH.COO.Ph	Related to IV
IX,	Phenyl α-methylacrylate	CH_2:CMe.COO.Ph	Related to IV
X,	Phenyl formate	H.COO.Ph	Product of VIII and IX
XI,	Styrene	CH_2:CHPh	Product of VIII
XII,	α-Methylstyrene	CH_2:CMePh	Product of IX
XIII,	Ethylene diacrylate	CH_2:CH.COO.CH_2 CH_2:CH.COO.CH_2	Model for II
XIV,	Vinyl acrylate	CH_2:CH.COO.CH:CH_2	Product of II and XIII

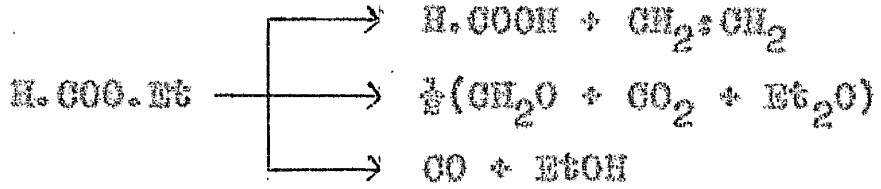
Table 1(Contd.)- Pyrolysands studied qualitatively and semi-quantitatively.

	Pyrolysand	Structure	Relationship to I
XV,	Methyl fumarate	Me.OOC.CH:CH.COO.Me (trans)	Model for II
XVI,	Methyl crotonate	MeCH:CH.COO.Me (cis)	Product of XV and XII
XVII,	Crotonaldehyde	MeCH:CH.CHO (cis)	Product of XV and XIX
XVIII,	Methyl acrylate	CH_2:CH.COO.Me	Product of XV and XII
XIX,	Methyl maleate	Me.OOC.CH:CH.COO.Me (cis)	Related to XV
XX,	Fumaric acid	HOOC.CH:CH.COOH (trans)	Product of II
XXI,	Poly(neo-pentylene fumarate)	-OOC.CH:CH.COO.CH_2.CMe_2.CH_2- (trans)	Related to II
XXII,	Poly(p-phenylene fumarate)	-OOC.CH:CH.COO. (trans)	Related to II
XXIII,	Poly(methyl fumarate - methyl α-methylacrylate	A copolymer	Model for I; related to III
XXIV,	Poly(neo-pentylene fumarate - methyl α-methylacrylate	As in Figure 1, neo-pentylene replacing ethylene units	Related to I

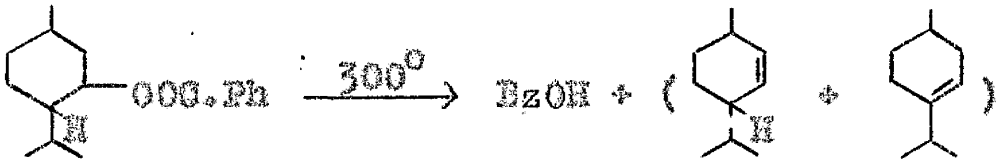
Table 2- Pyrolysands studied for threshold temperature determination.

	Pyrolysand	Structure	Relationship to I
I,	Poly(ethylene fumarate - methyl α-methylacrylate	See Figure 1	
II,	Poly(ethylene fumarate)	-OOC.CH:CH.COO.CH_2.CH_2- (trans)	Polyester chain
III,	Poly(methyl α-methylacrylate)	-CH_2.C.Me- COO.Me	α-Methylacrylate chain
XXI,	Poly(neo-pentylene fumarate)	-OOC.CH:CH.COO.CH_2.CMe_2.CH_2- (trans)	Related to II
XXII,	Poly(p-phenylene fumarate)	-OOC.CH:CH.COO. (trans)	Related to II
XXIII,	Poly(methyl fumarate - methyl α-methylacrylate	A copolymer	Model for I; related to III
XXIV,	Poly(neo-pentylene fumarate - methyl α-methylacrylate	As in Figure 1, neo-pentylene replacing ethylene units	Related to I
XXV,	Ethyl fumarate	CH_3.CH_2.OOC.CH:CH.COO.CH_2.CH_3 (trans)	Model for I
XXVI,	Ethyl maleate	CH_3.CH_2.OOC.CH:CH.COO.CH_2.CH_3 (cis)	Related to XXV
XXVII,	Ethyl succinate	CH_3.CH_2.OOC.CH_2.CH_2.COO.CH_2.CH_3	Model for I (cross-linking points)
XXVIII,	Ethyl adipate	CH_3.CH_2.OOC.$(CH_2)_4$.COO.CH_2.CH_3	Models for saturated dibasic acid units
XXIX,	Ethyl sebacate	CH_3.CH_2.OOC.$(CH_2)_8$.COO.CH_2.CH_3	
XXX,	Poly(ethylene succinate)	-OOC.CH_2.CH_2.COO.CH_2.CH_2-	Related to II

routes. For example, ethyl formate was in 1897 reported by Engler and Grimm[10] to yield ethylene and formic acid by an exclusive route, but later workers[11] have shown this to be but one, the major, of three primary competitive routes:



The literature does, however, contain one well-established example of an exclusive breakdown route in the pyrolysis of (-)-menthyl benzoate reported by Barton[12]:



Recent work at higher temperatures by Muir and Ritchie[13] has confirmed that this route is indeed exclusive.

Early reports of exclusive breakdown routes may frequently be attributed to non-detection of minor products, or possibly to confusion of primary and secondary products. The competitive routes now elucidated depend qualitatively upon the structure of the molecule and quantitatively upon pyrolysis conditions. Hurd[14] quotes a number of generalisations on pyrolytic breakdown to which, however, there are so many exceptions that they are of little value in predicting

the nature of breakdown of a compound. A review of the literature indicates that most ester breakdown routes can be classified as one of the following types, the nomenclature for which was devised by Ritchie[15]. From these established routes it is possible to predict to some extent the probable breakdown of various types of esters.

1.1.1. Alkyl-oxygen scission (A^1, A^0).

A^1 is almost invariably the predominating route in breakdown of esters with an available β-hydrogen atom on the alkyl group. Scission between the alkyl group and the ether oxygen atom with migration of the hydrogen atom to the carboxyl group yields an acid and an olefin. Under appropriate conditions the reaction occurs very smoothly and has long been employed in syntheses of complex α-unsaturated hydrocarbons, as for example, the production of hexadecene by pyrolysis of cetyl palmitate[16].

$$C_{15}H_{31}\cdot COO\cdot(CH_2)_{15}Me \longrightarrow C_{15}H_{31}\cdot COOH + CH_2{:}CH(CH_2)_{13}Me \quad \ldots A^1$$

Recent work by Bailey and King[17] has yielded olefins by pyrolysis of alkyl acetates. For instance:

$$Me\cdot COO\cdot \underset{\displaystyle CH_3}{\underset{|}{CH}}CHMe_2 \longrightarrow Me\cdot COOH + CH_2{:}CHCHMe_2 \quad \ldots A^1$$

This ester contains two available β-hydrogen atoms,

each of which would yield a different olefin if involved in A^1. In the absence of carbonisation, which has been shown to cause isomerisation[18], Bailey and King[17] found 3-methylbut-1-ene to be formed exclusively by migration of the β-hydrogen atom from the methyl group, as above. There was no evidence for the formally possible 3-methylbut-2-ene;

$$\mathrm{Me.COO.CH(Me)CHMe_2} \xrightarrow{?} \mathrm{Me.COOH} + \mathrm{MeCH{:}CMe_2} \quad \ldots A^1$$

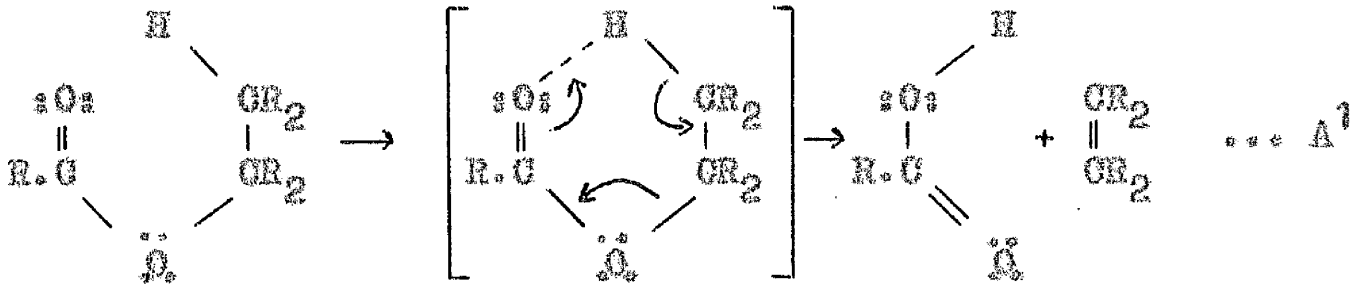
There are two rules which might indicate the olefin favoured in A^1 of such esters. The Saytseff rule[19] states that the decomposition of alkyl halides yields mainly the more highly branched hydrocarbon, while on the other hand the Hoffman rule[19] states that in dehydration of quaternary ammonium hydroxides the olefin with fewer attached alkyl groups is favoured. Bailey *et al.*[17,20] found the Hoffman rule to be consistently followed in pyrolysis of alkyl acetates, though the corresponding alcohols dehydrated in accordance with the Saytseff rule.

Other workers have observed a mixture of two possible isomeric olefins, as for example, but-1-ene and but-2-ene from *sec.*-butyl acetate[21];

$$\mathrm{MeCH(CH_2Me).OAc} \xrightarrow{-\mathrm{AcOH}} \mathrm{CH_2{:}CHCH_2Me} + \mathrm{MeCH{:}CHMe} \quad \ldots A^1$$

In such examples the possibility of isomerisation following scission must be considered.

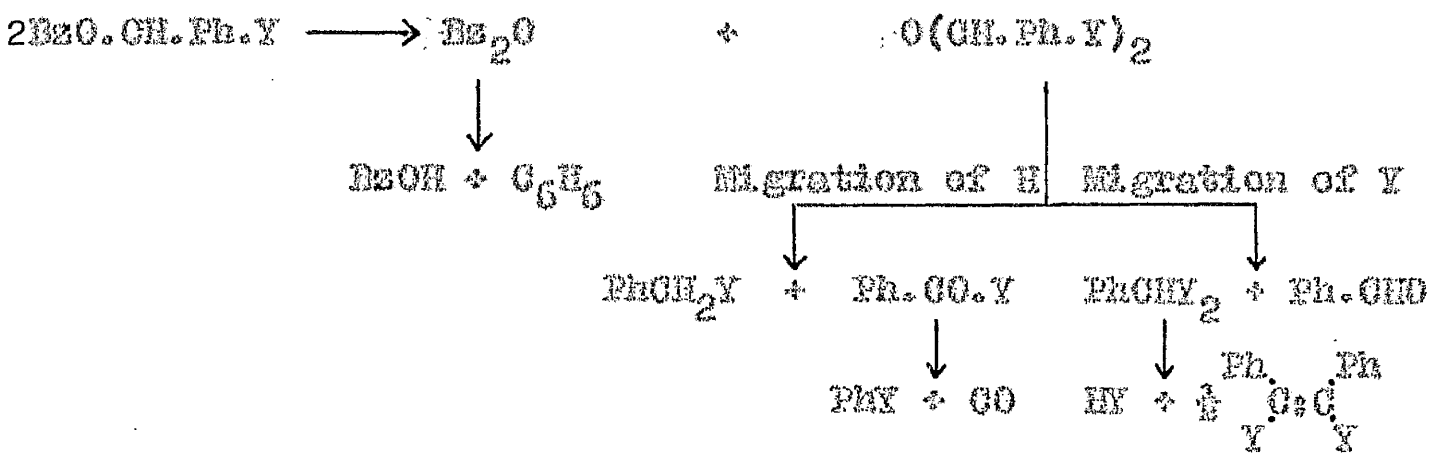
Hurd and Blunck[22] have proposed for A^1 a mechanism which, though criticised by Houtman et al.[21], is now generally accepted. They suggest that a transient six-membered ring, involving bonding of the β-hydrogen atom, is formed before scission:



A^0 designates alkyl-oxygen scission in esters possessing an α- but not a β-hydrogen atom. Thus, Peytral[23] has shown methyl acetate to yield acetic acid and ethylene:

$$Me.COO.Me \longrightarrow Me.COOH + \tfrac{1}{2}CH_2{:}CH_2 \qquad \ldots A^0$$

Jones and Ritchie[24] have observed that α-substituted benzyl benzoates yield an acid and an olefin, but attribute their formation to secondary breakdown subsequent to the following minor competitive primary scission:



(Y = Br, CN)

It is thought possible that in the uncommon A^0 reaction the olefin is formed by combination of two transient $:CR^1R^2$ diradicals.

1.1.2 Alkenyl-oxygen scission (A^2).

α-β-alkenyl esters yield an alkyne by A^2 in a manner similar to olefin formation by A^1 of alkyl esters. The literature contains no early examples but Allen, Forman and Ritchie[25] have observed the reaction in pyrolysis of vinyl carboxylates:

$$BzO.CH:CH_2 \longrightarrow BzOH + CH:CH \quad \ldots A^2$$

$$CHR^1R^2COO.CH:CH_2 \longrightarrow CHR^1R^2COOH + CH:CH \quad \ldots A^2$$

($R^1 = R^2 = H$; $R^1 = R^2 = Me$)

A^2 is generally a minor competitive route. It is believed that it may occur by a mechanism similar to that of A^1, but less readily because of the weakening influence of

the adjacent unsaturation on the hydrogen bond formed in the cyclic intermediate.

1.1.3. Acyl-oxygen scission (B^1,B^2).

In esters where A^1 is precluded through lack of an available β-hydrogen atom, scission between the acyl group and the other oxygen atom may occur. Migration of a hydrogen atom occurs from the acyl to alkoxy group (B^1) or from the alkoxy to the acyl group (B^2).

B^2 is precluded in aryl esters, where B^1 yields a keten and an alcohol as in pyrolysis of phenyl acetate[22]:

$$Me.COO.Ph \longrightarrow CH_2:CO + PhOH \quad \ldots B^1$$

Though B^2 is formally possible in breakdown of the alkenyl ester vinyl isobutyrate, acyl-oxygen scission products corresponding to a B^1 reaction only have been found[25]:

$$Me_2CH.COO.CH:CH_2 \longrightarrow [CH_2:CHOH] + [Me_2C:CO] \quad \ldots B^1$$

$$[CH_2:CHOH] \downarrow \rightarrow Me.CHO$$

$$[Me_2C:CO] \rightarrow MeCH:CH_2 + CO$$

$$[Me_2C:CO] \rightarrow \tfrac{1}{2}(Me_2C:CMe_2) + CO$$

There is no doubt that acetaldehyde results, via its enol form, from a B^1, and the other observed products may be attributed to secondary breakdown of dimethylketen by the established[26] routes shown.

B^2 is a reversal of the Tischenko reaction[27], an ester yielding two similar or dissimilar aldehyde molecules. It is a common route in pyrolyses of esters lacking an available β-hydrogen atom to take part in A^1. (1) Benzyl benzoate[26] and (2) methyl acetate[23] are examples:

(1) $PhCO.OCH_2Ph \longrightarrow 2Ph.CHO$ ... B^2

(2) $Me.COO.Me \longrightarrow Me.CHO + CH_2O$ ... B^2

In breakdown of ethyl acetate, Hurd and Blunck[22] have observed products which may be attributed to competitive A^1, B^1 and B^2 reactions:

$$Me.COO.Et \longrightarrow \begin{cases} Me.COOH + CH_2{:}CH_2 & \ldots A^1 \\ CH_2{:}CO + EtOH & \ldots B^1 \\ 2Me.CHO & \ldots B^2 \end{cases}$$

This is apparently the only report of competitive B^1 and B^2, B^1 being generally confined to alkenyl and aryl and B^2 to alkyl esters. Engler and Low[29], however, report that methyl phenylacetate (360°, sealed tube) yields toluene and methanol, which may now be attributed with other products overlooked, possibly because of their further breakdown, to competitive B^1 and B^2:

$$PhCH_2.COO.Me \longrightarrow \begin{cases} [PhCH{:}CO] + MeOH & \ldots B^1 \\ [PhCH_2.CHO] + [CH_2O] & \ldots B^2 \end{cases}$$

$$PhCH_2 + CO$$

(Other observed products: carbon dioxide, methane)

The postulated decarbonylation of benzylaldehyde is in accordance with the breakdown of aldehydes in general[14,30] and also partially explains the observed carbon monoxide.

The mechanism of acyl-oxygen scission has not yet been elucidated.

1.1.4. Decarbonylation (C^1).

The literature contains few examples of ester C^1 and these few are confined mainly to formates, which also possess the aldehyde functional group and might therefore be expected to decarbonylate[14,30]. C^1 in formates may also in some respects be considered as a special case of B^1, migration of the hydrogen atom to the alkoxy group leaving simply carbon monoxide:

$$H.COO.R \longrightarrow CO + ROH \quad \ldots C^1(n^1)$$

Adickes et al.[31] report that phenyl formate, in which both A^1 and B^2 are precluded, decomposes exclusively by C^1 on distillation even at reduced pressure:

$$H.COO.Ph \longrightarrow CO + PhOH \quad \ldots C^1$$

Similarly, carbon monoxide and small amounts of methanol and ethanol in the pyrolysates from methyl formate[32] and ethyl formate[11] respectively are attributable to C^1. van Romburgh[33] obtained quantitative yields of pentaerythritol

in pyrolysis of its tetraformate at 220-230°:

$$C(CH_2OOC.H)_4 \longrightarrow 4CO + C(CH_2OH)_4 \quad \ldots\ C^1$$

One example of C^1 in esters other than formates is the competitive breakdown of ethylene oxalate to ethylene carbonate reported by Milicheev[34]:

$$\begin{matrix} COO.CH_2 \\ | \quad | \\ COO.CH_2 \end{matrix} \longrightarrow CO + CO\begin{matrix} O.CH_2 \\ \diagdown \\ \diagup \\ O.CH_2 \end{matrix} \quad \ldots\ C^1$$

Carbon monoxide observed in the pyrolysate from ethyl pyruvate would be expected to result from elimination of the keto group, but by introducing the isotope ^{14}C Calvin and Lemmon[35] have shown it to derive instead from the ester carbonyl group:

$$Me.{}^{14}CO.COO.Et \longrightarrow CO + \text{traces } CO_2 + {}^{14}C \text{ by-products} \quad \ldots\ C^1$$

This reaction is therefore a true case of ester C^1, though the mechanism is obscure. In other cases where carbon monoxide is an ester pyrolysis product it can be attributed to secondary C^1 of carbonyl products[14,30] as in breakdown of methyl acetate[23]:

$$Me.COO.Me \longrightarrow \underset{\downarrow}{Me.CHO} + \underset{\downarrow}{CH_2O} \quad \ldots\ B^2$$

$$CO + CH_4 \ldots C^1; \qquad CO + H_2 \ldots C^1$$

1.1.5. Decarboxylation (C^2).

Although C^2 of carboxylic acids is well-established[14],

the literature contains only a few early examples of ester c^2 such as that following[36]:

$$\begin{matrix} CH.COO.Ph \\ \| \\ CH.COO.Ph \end{matrix} \xrightarrow{-CO_2} PhCH{:}CH.COO.Ph \xrightarrow{-CO_2} PhCH{:}CHPh \ldots c^2,c^2$$

(cis or trans) (trans)

Recent work in these laboratories, however, has shown that c^2 is a general reaction in breakdown of esters with an α-unsaturated acyl or alkoxy group. It has been observed in pyrolysis of (1) vinyl benzoate[25] (olefinic and benzenoid α-unsaturation), (2) vinyl acetate and vinyl iso-butyrate[25] (olefinic α-unsaturation) and (3) αα-dicyanobenzyl benzoate[37] (benzenoid α-unsaturation):

(1) $Bz.O.CH{:}CH_2 \longrightarrow PhCH{:}CH_2 + CO_2 \ldots c^2$

(2) $CHR^1R^2.COO.CH{:}CH_2 \longrightarrow CHR^1R^2CH{:}CH_2 + CO_2 \ldots c^2$

($R^1 = R^2 = H$; $R^1 = R^2 = Me$).

(3) $Bz.O.CPh(CN)_2 \longrightarrow CPh_2(CN)_2 + CO_2 \ldots c^2$

Of other esters only formates have been reported to undergo c^2. For example[38], (1) dihydrocholesteryl formate and (2) myricyl formate yield cholestane and triacontane respectively (290°, 100 mm.):

(1) $H.COO.C_{27}H_{47} \longrightarrow C_{27}H_{48} + CO_2 \ldots c^2$

(2) $H.COO.C_{30}H_{61} \longrightarrow C_{30}H_{62} + CO_2 \ldots c^2$

In contrast to phenyl formate[31], triphenylmethyl formate[39] undergoes not O^1 but O^2:

$$H.COO.CPh_3 \longrightarrow CHPh_3 + CO_2 \quad \ldots O^2$$

Lactones, possessing an internal ester structure, also undergo O^2 in absence of α-unsaturation. Little information is available on δ- and γ-lactones, but the reaction has been shown to be general for ε-lactones[40]:

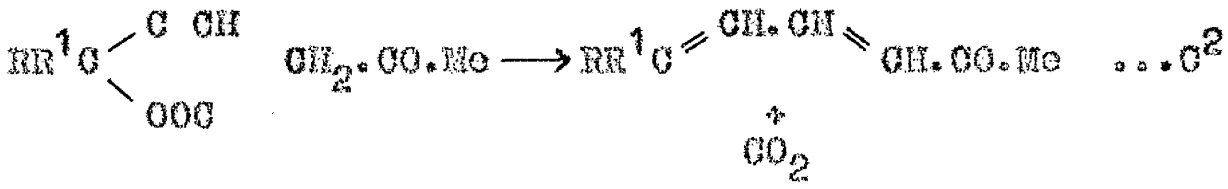
$$\begin{matrix} R^1R^2C \\ | \\ R^1R^2C \end{matrix} \cdot \begin{matrix} CO \\ | \\ O \end{matrix} \longrightarrow R^1R^2C{:}CR^1R^2 + CO_2 \quad \ldots O^2$$

Only two examples of O^2 not represented in the above cases are recorded. Filicheev[41] claims that ethylene succinate decarboxylates competitively to ethylene:

$$\begin{matrix} CH_2.COO.CH_2 \\ | \qquad\quad | \\ CH_2.COO.CH_2 \end{matrix} \longrightarrow 2\ CH_2{:}CH_2 + 2\ CO_2 \quad \ldots O^2$$

A study of the original paper, however, suggests that Filicheev may have been dealing with poly(ethylene succinate) rather than the cyclic monomer. Korshak and Rogozhin[42] have observed carbon dioxide evolution in preparation of this polyester from succinic acid and ethylene glycol, and repetition of Filicheev's work under stricter conditions is necessary before it can be accepted as an exception to the general rule of O^2 only in α-unsaturated esters, certain formates and ε-lactones.

The second example concerns acetoacetates of ethynylcarbinols and is apparently a true exception to the general rule. Lacey[43] has reported such esters to decarboxylate to the corresponding dienones:

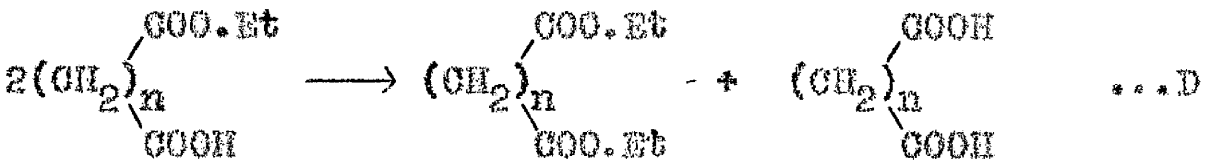


...C[2]

No acceptable general mechanism has been postulated for elimination of carbon dioxide from an ester molecule. In formates it involves simply migration of a hydrogen atom and in β-lactones leaves already formed the carbon skeleton of the residual product. In α-unsaturated esters, there is no plausible molecular explanation of the reaction and in this case the possibility of a free radical mechanism must be considered.

1.1.6. Disproportionation (D).

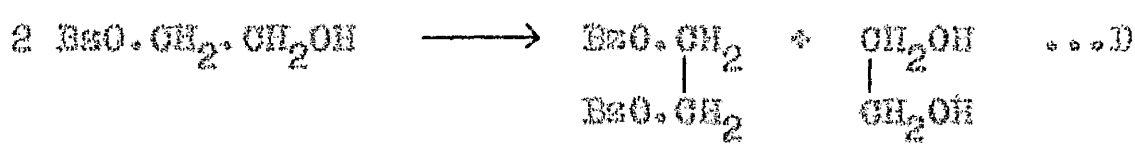
D is common in breakdown of inorganic esters[14] and is frequently exhibited by monoesters of organic dibasic acids or alcohols, where products of greater symmetry are formed. Thus, (1) monoethyl succinate[44] and (2) monoethyl sebacate[45] yield the corresponding diester and acid on distillation:



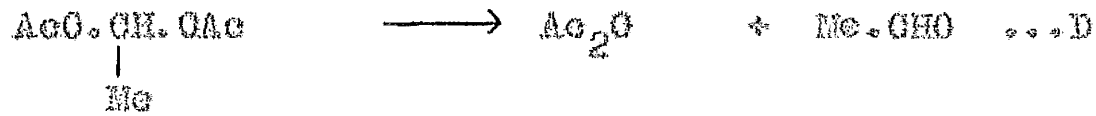
...D

(1) n = 2; (2) n = 8.

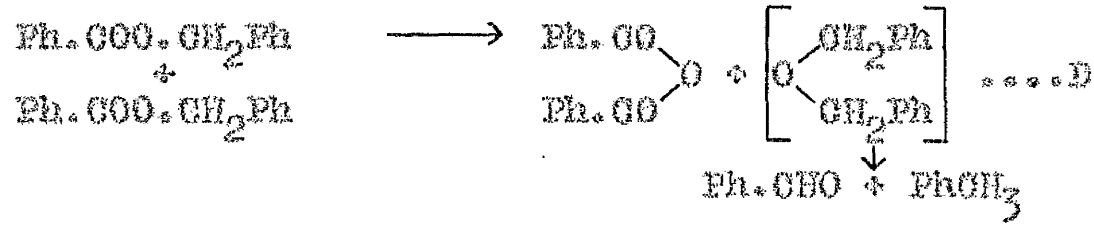
Gretcher and Pittinger[46] have shown monoaryl esters of ethylene glycol to yield the diester and ethylene glycol, as has been confirmed by Iengar and Mitchie[47] for 2-hydroxyethyl benzoate on distillation:



Genther[48] has recorded a different type of D in the breakdown of ethylidene diacetate to acetic anhydride and acetaldehyde on distillation:



Hurd and Bennett[23] postulate a D reaction to account for products observed with benzaldehyde (attributable mainly to a competitive primary B^2) in pyrolysis of benzyl benzoate:



Though D is perhaps predictable in pyrolysis of monoesters of dibasic acids or alcohols, there is no obvious general mechanism for the reaction.

1.1.7. Rearrangement (R).

An ester molecule may rearrange to a more stable form on pyrolysis, the simplest and most obvious example of such

a reaction being geometric isomerisation. The conversion of (1) phenyl oleate to phenyl elaidate[49] and (2) dibenzyl maleate to dibenzyl fumarate[50] occurs on heating above the melting points:

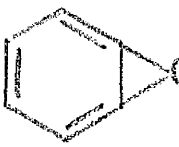
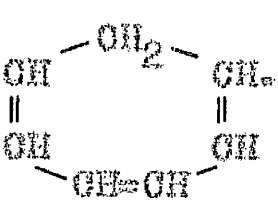
(1) $\begin{matrix} HC(CH_2)_7Me \\ \| \\ HC(CH_2)_7.COO.Ph \end{matrix} \longrightarrow \begin{matrix} HC(CH_2)_7Me \\ \| \\ Ph.OOC.(CH_2)_7CH \end{matrix}$ ...R

(2) $\begin{matrix} HC.COO.CH_2Ph \\ \| \\ HC.COO.CH_2Ph \end{matrix} \longrightarrow \begin{matrix} HC.COO.CH_2Ph \\ \| \\ PhH_2C.OOC.CH \end{matrix}$ ...R

Pyrolytic R of an ester molecule may also yield an entirely different structure of lower energy content. Thus, phenyl cyclohexanecarboxylate rearranges to o-hydroxyphenyl cyclohexyl ketone[51], this being a Fries-type reaction promoted by heat alone:

$C_6H_{11}.COO.Ph \longrightarrow$  ...R

Ethyl cycloheptatrienecarboxylate is formed by heating ethyl pseudophenylacetate (150°, 4 hours)[52]:

 $CH.COO.Et \longrightarrow$  ...R

An early report by Maligenus[53] of enol carboxylates

rearranging to β-diketones has been confirmed by Young et al.[54]:

$$R^1.COO.Me:CHR^2 \longrightarrow R^1.CO.CHR^2.CO.Me \quad \ldots R$$

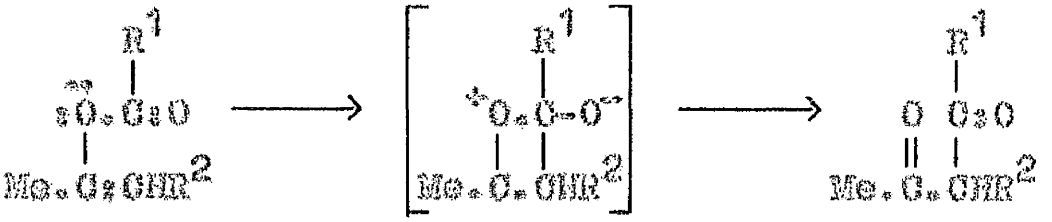
(51; R^1=Me, COO.Et; R^2=H. 52; R^1=Me, Ph; R^2=H).

Similarly, Allan and Ritchie[55] have observed R of cyclohex-1-enyl benzoate to 2-benzoylcyclohexanone, and Allan, Forman and Ritchie[25] R of vinyl carboxylates to β-ketonaldehydes, which they did not isolate since they are unstable, but to which they attribute carbon monoxide and ketone products:

$$R.COO.CH:CH_2 \longrightarrow \left[R.CO.CH_2.CHO\right] \quad \ldots R$$
$$\downarrow$$
$$R.CO.Me + CO \quad \ldots O^1$$

(R = Me, Ph, $CHMe_2$).

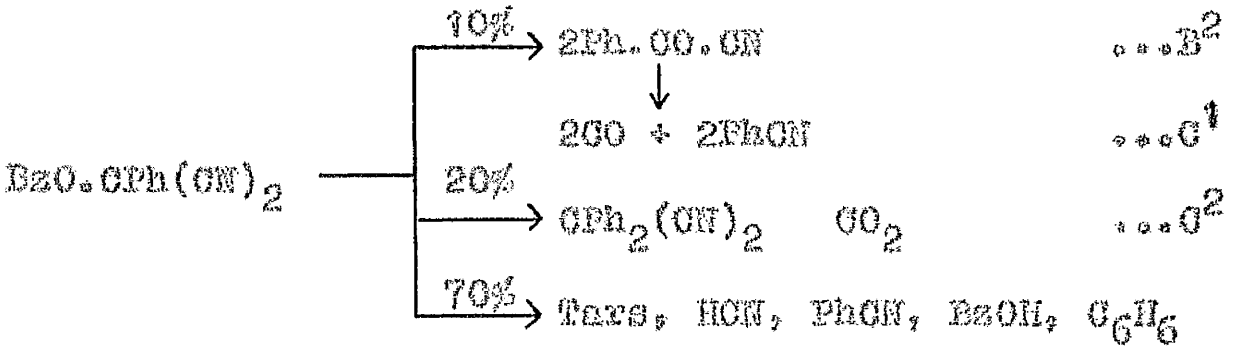
Young et al.[54] have proposed an acceptable mechanism for R in enol carboxylate pyrolysis, suggesting that reaction occurs via a cyclic transition state:



1.1.6. Other pyrolytic routes and carbonisation.

There are examples of pyrolysis products which cannot satisfactorily be attributed to any of the above routes.

For example, there is the production of benzaldehyde from methyl phenylacetate[29] and of hydrogen cyanide, benzoic acid and benzene from α-dicyanobenzyl benzoate in accordance with the following scheme proposed by Bennet et al.[37]:

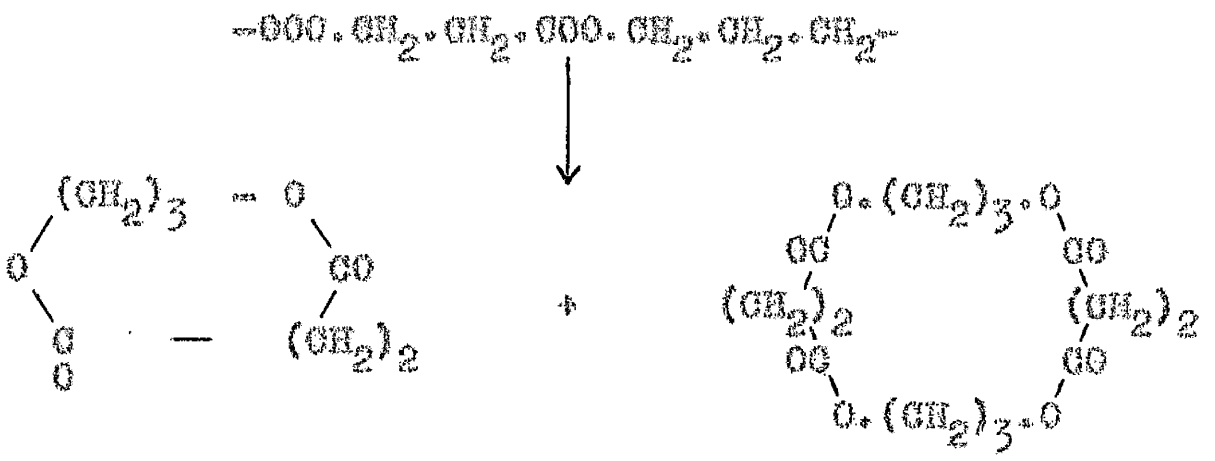


In these and other pyrolyses where there is no acceptable molecular mechanism to explain the observed products, there may be some free radical mechanism. Hurd and Blunck[22] propose a free radical mechanism in esters lacking an available β-hydrogen atom, while Bilger and Hibbert[56] have suggested that all pyrolytic reactions involve free radicals.

The formation of tarry or carbonaceous materials as in the above scheme is frequently encountered. The mechanism has not been investigated, there being considerable difficulties in analysis of the complex tars. Bailey and Rosenberg[18] have shown carbonisation to catalyse isomerisation of olefins and the whole subject of their rôle in pyrolysis is worthy of investigation.

1.2. The Pyrolysis of Linear Polyesters.

Though no previous work has been done on the thermal degradation of polyfumarates, some other linear polyesters have been studied. Carothers *et al.*[57] report that polycarbonates and other saturated polyesters, in alkaline conditions and in presence of inorganic chloride catalysts, yield mainly cyclic monomer and dimer type products:



Considerable work has been done on the fibre-forming poly(ethylene terephthalate), which yields not cyclic products but chain fragments and low-molecular weight compounds. Pohl[58] deduced a random chain scission, the β-hydrogen atoms being involved in A^1 reactions within the chain; Marshall and Todd[59] also deduced random chain scission and offered evidence that the A^1 reaction is free radical in character. Later work by Ritchie *et al.*[47,60] questions the validity of Pohl's experimental deductions, though it is not claimed that the reaction is not random.

It is clear from Ritchie's recent work[25,47,60] that the observed pyrolysis products may be attributed to breakdown of the polyester by the routes already described for simple esters (pp.9-22) and that information derived from the study of model compounds representing segments of the chain may be satisfactorily applied to poly(ethylene terephthalate) itself.

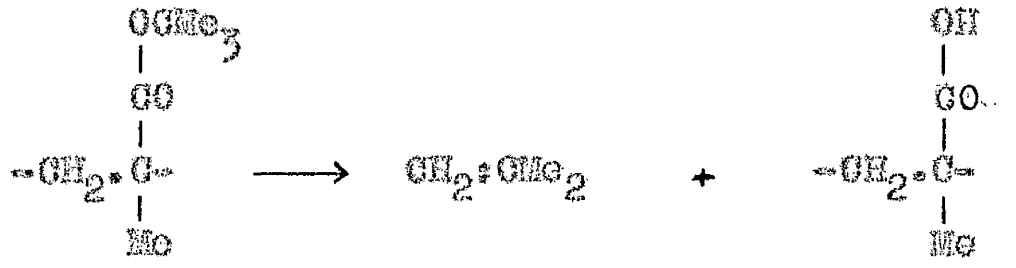
1.3. The Pyrolysis of Linear Addition Polymers.

Much of the knowledge on pyrolysis of linear addition polymers derives from Grassie, who describes his own and other relevant work in "The Chemistry of High Polymer Degradation Processes"[7]. It is pointed out that such polymers, which unlike polycondensates can formally revert to monomer on pyrolysis, may be divided into two fairly rigid classes - (1) those which yield monomer or related products and (2) those which do not.

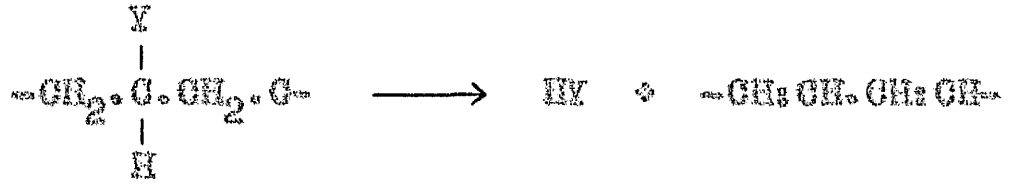
(1) Monomer formation results from a free radical depolymerisation which is facilitated in quaternary carbon atom structures and also in polystyrene by resonance - conferred stability in the radical. Polymers in this class generally have a low heat of polymerisation (less than ca. 10 k.cal./mole). They must therefore tend more readily to yield monomer on pyrolysis, since the endothermic depolymerisation reaction is the exact opposite of the exothermic propagation step which determines the heat

of polymerisation.

(2) In the second group depolymerisation does not occur; there is instead a reaction involving removal of chain substituents and leaving a polymer of altered constitution. Grassie describes the elimination of isobutene from poly(tert.-butyl α-methylacrylate), forming one α-methylacrylic acid chain unit per molecule eliminated by an A^1 reaction:



This is an exception to the general behaviour of poly(α-methylacrylates) and does not apply to poly(methyl α-methylacrylate) (below, Section 1.4.). It is typical of vinyl polmer degradation, where for example, hydrogen chloride and acetic acid are volatilised from poly(vinyl chloride) and poly(vinyl acetate) respectively, leaving a polyacetylene residue:



(Y = Cl, OOO.Me).

1.4. The Pyrolysis of Polymers and Copolymers of Methyl α-Methylacrylate.

Poly(methyl α-methylacrylate) falls in the first group; under appropriate conditions it yields up to 90% monomer. Votinov et al.[61] deduced a random chain scission reaction, but Grassie and Melville[62] later showed this to be wrong and proved monomer to be liberated by a free radical depolymerisation of separate chains, so that the molecular weight of the polymer residue at any stage is not appreciably altered from the original value. Grassie[7] reports depolymerisation to be initiated at unsaturated end-groups formed by disproportionation termination of polymerisation. At 220° he obtained a monomer yield corresponding to the percentage of chains with at least one unsaturated end in peroxide and photo-catalysed polymers, and in samples polymerised in benzene where chain transfer limits the number of unsaturated ends.

In cross-linked systems formed by copolymerisation of methyl α-methylacrylate with small amounts of ethylene αα-dimethylacrylate Grassie found little alteration in the depolymerisation, each αα-dimethylacrylate behaving like an α-methylacrylate unit. Very different behaviour was observed in behaviour of methyl α-methylacrylate - acrylonitrile copolymers. Grassie deduced in this case an initial

chain scission in the region of the acrylonitrile units; he suggests that thereafter disproportionation occurs between acrylonitrile and α-methylacrylate units, forming a depolymerisation-initiating chain end. Depolymerisation is then thought to be terminated at the inclusion of the next acrylonitrile unit.

2. DISCUSSION OF RESULTS

2.1. Qualitative and Semi-Quantitative Pyrolysis.

The pyrolysands listed in Table 1 are discussed in this section. The apparatus used is described in Section 3.1. Flow pyrolysis conditions are summarised in Table 10, Section 3.3., and analytical results in Tables 11-17, Section 3.3.; relevant data on static pyrolyses is contained in Tables 18 and 19, Section 3.3.

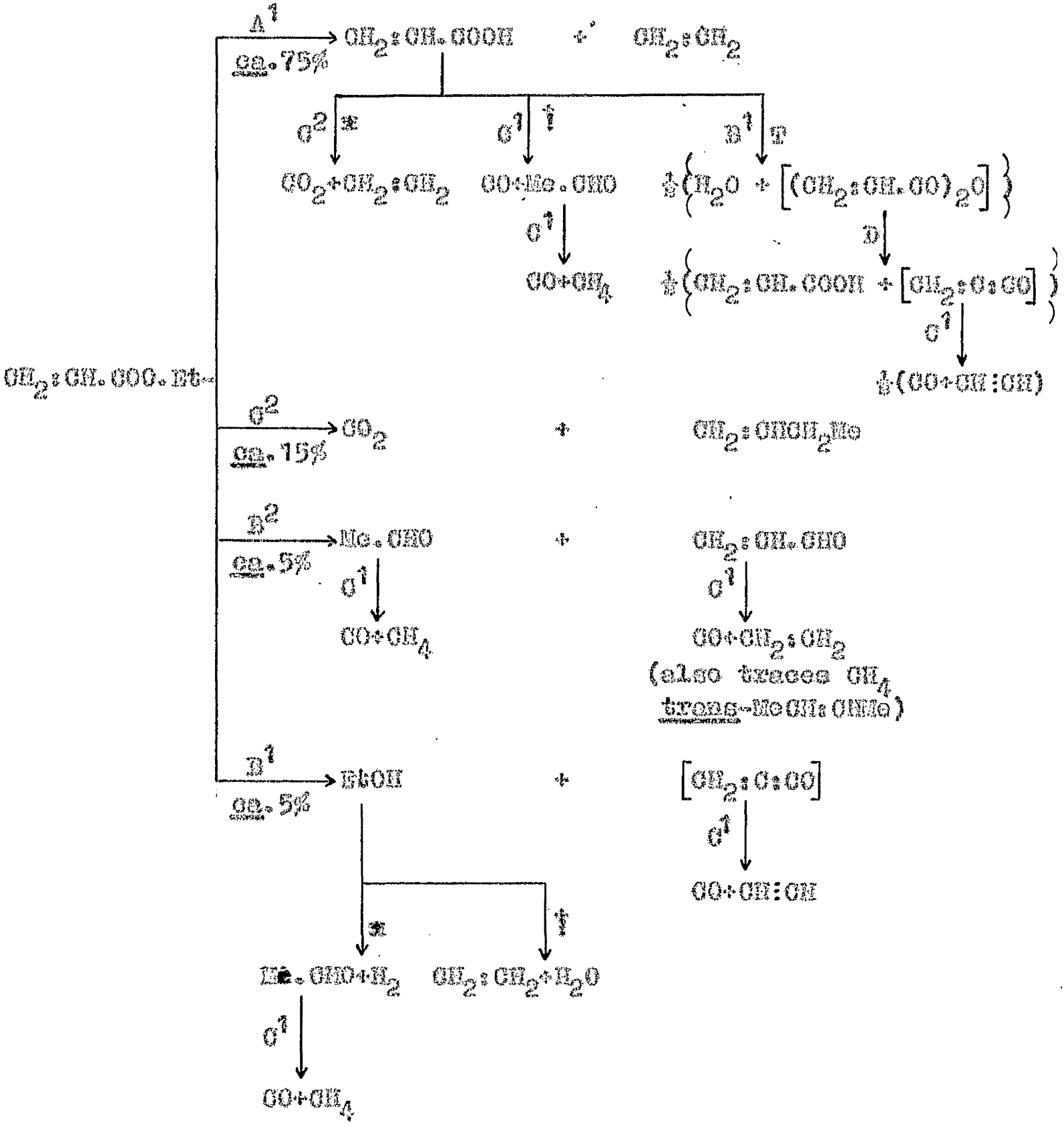
2.1.1. The pyrolysis of ethyl acrylate and related compounds.

Ethyl acrylate (IV).

Itself a very simple model compound for poly(ethylene fumarate) (II), IV was also studied to furnish information on the breakdown of a simple alkyl acrylate before undertaking the pyrolysis of ethylene diacrylate (XIII), a more realistic model for II.

At 500° in a Pyrex glass flow-reactor IV decomposes to the extent of ca. 95% (Table 10, runs 2-5). As is predictable, the major scission is A^1; there are also competitive C^2, B^1 and B^2 reactions. The following scheme shows what is believed to be the complete primary, secondary and tertiary breakdown. All products with the exception of those shown in square brackets were identified and the weight

contribution of competitive primary routes to the overall



breakdown estimated. The extent of secondary breakdown

routes is indicated as major (*), minor (†) or trace (?).

The results agree with and amplify an earlier report by Hatchford et al.[63] who did not, however, specify any reactions other than A^1. The predominance of A^1 calls for no comment, while of the other competitive routes now elucidated C^2, yielding but-1-ene, is in line with previous work on α-unsaturated esters[25,36,37]. There is only one reported precedent of B^1 in an alkyl ester[22, p.14]; in the present case it offers the only acceptable explanation of the formation of ethanol. The postulated accompanying product methylenecketen, a compound not recorded in the literature, was not detected; it is thought to be so unstable as to break down on formation to carbon monoxide and acetylene. This point is pursued in a later Section (p.33). Acraldehyde in the pyrolysate from IV confirms the predictable B^2 scission, also responsible in part for acetaldehyde formation. Methane traces are attributable to the established C^1 of acetaldehyde[30].

The foregoing reaction scheme was confirmed both qualitatively and semi-quantitatively by separate pyrolyses under similar conditions of the following primary products:

Acrylic acid (V).

V decomposes to the extent of ca.25% (Table 10, run 6), the major route being as expected[14] C^2 yielding ethylene.

Acetaldehyde may be accounted for only by a minor C^1, and water, acetylene and (in part) carbon monoxide by breakdown subsequent to both B^1 and anhydride formation.

Unlike C^2, C^1 is not an established route in acid pyrolysis, the only previously recorded example being that of benzoic acid[64]:

$$BzOH \longrightarrow CO + PhOH \quad \ldots C^1$$

As in breakdown of V, C^1 in benzoic acid is of a minor extent accompanying a major C^2. Both acids are α-unsaturated and this may in some way facilitate the mechanism of C^1.

The B^1 reaction postulated to account for the major part of the water in the pyrolysate from V has no precedent. Should this be the only water-forming route, then α-methylacrylic acid, in which B^1 is precluded, would predictably yield no water. Later work by Forman[65] showed that α-methylacrylic acid does in fact yield traces of water. Since it is improbable that two such similar acids yield water by entirely different reactions, anhydride formation common to both is postulated. No anhydride was detected in the pyrolysate from V, nor was any by Forman, but Brown and Ritchie[66] have shown acrylic anhydride to be unstable and yield products common to other intermediates in the pyrolysis of V:

$$2\ (CH_2{:}CH.CO)_2O \longrightarrow CH_2{:}CH.COOH + \left[\begin{array}{l} CH{:}C.CHO \\ \downarrow \\ CO{+}CH{:}CH \end{array}\right] \quad \ldots C^1$$

Acrylic anhydride can thus readily escape detection. Its formation and subsequent decomposition as shown in the reaction scheme is analogous to the pyrolysis of acetic acid, in which Damford and Dewar[67] observed keten as a product. Swaare and Murawski[68] later showed keten to be formed *via* the anhydride:

$$2\ Me.COOH \longrightarrow H_2O + (Me.CO)_2O \downarrow \tfrac{1}{2}(Me.COOH + CH_2:CO)$$

In line with this work, the precursor of acetylene and carbon monoxide in the pyrolysates from both V and VI is postulated as methylenekoten, rather than propiolic aldehyde as proposed by Brown and Ritchie[66]. This aldehyde has been shown[69] to decarbonylate readily to acetylene, but since neither it nor the keten was isolated it is impossible to state which is the true intermediate. Isomerisation may precede decomposition; the conjugated structure of the aldehyde is likely to be rather more stable than the cumulative keten structure:

$$CH_2:C:C:O \rightleftharpoons CH:O.C:O \quad (H) \downarrow CO + CH:CH \qquad \ldots(1)$$

V yielded measurable amounts of water; α-methylacrylic acid yielded only traces[65]. It is therefore held that both yield traces *via* anhydride formation and that in pyrolysis of V the yield is greatly increased by the occurrence of the

E^1 reaction.

Acraldehyde (VI).

Decomposition of VI occurs to the extent of ca. 45% (Table 10, runs 7,8), exclusively by C^1. Breakdown did not, however, yield the theoretical equimolar quantities of carbon monoxide and ethylene, there being invariably a deficiency of the olefin. This deficiency, apparent in a paper by Allan, Jones and Ritchie[70], has been attributed by Thomson and Frewing[71] to the formation of hydrogen, methane, ethane and butenes, though no mechanism has been suggested. In the present work, methane and trans-but-2-ene were detected and are presumed to account for the ethylene deficiency. These products have been detected in pyrolysis of ethylene[72], but a report by Walker[73] indicates that under the working conditions here ethylene is stable. Furthermore, where ethylene is a product in breakdown of IV and V no deficiency was observed. From this and other evidence discussed below (p. 56), it is concluded that the olefin deficiency in pyrolysis of VI results from a primary reaction involving the aldehyde rather than from secondary breakdown of ethylene.

Ethanol (VII).

Two competitive routes comprise a total breakdown of ca. 30% in VII (Table 10, run 9). A major dehydrogenation

yields acetaldehyde and there is a minor dehydration to ethylene. Since the B^1 reaction yielding VII from the ester IV is itself a minor reaction, the major part of the water in the pyrolysate of IV must be formed *via* the acid V.

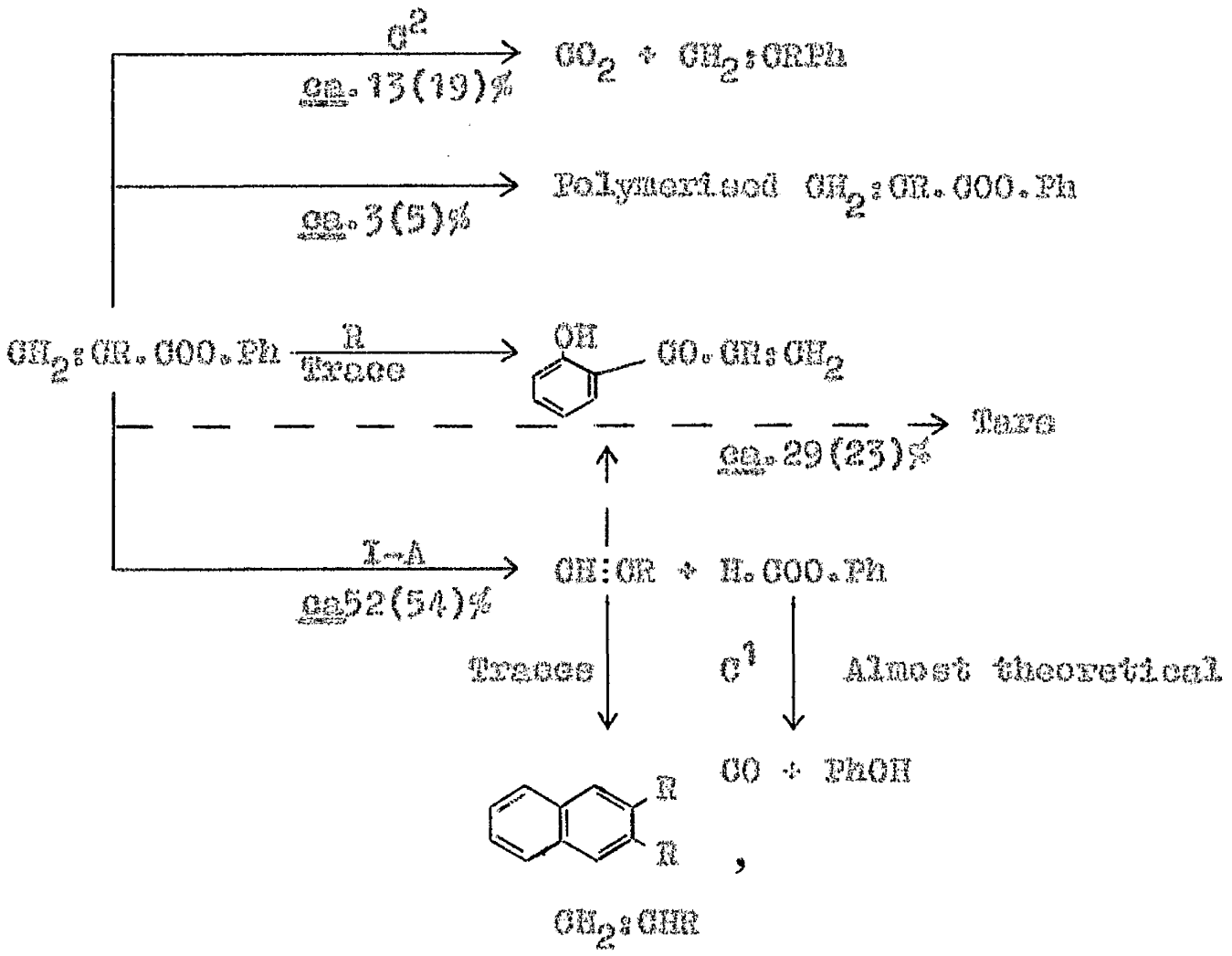
The following compounds related to IV were studied:

Phenyl acrylate (VIII) and phenyl α-methylacrylate (IX).

The predominance of A^1 in alkyl esters inhibits the investigation of other routes and for this reason the study of IV was extended to include pyrolysis of VIII. A concurrent study of IX was undertaken to help identify the rôle of the acyl α-hydrogen atom in pyrolysis of VIII.

Both VIII (R=H, below) and IX (R=Me, below) are very thermostable. Breakdown is almost negligible below 500° but above 600° both esters undergo pyrolysis with extensive carbonisation. At the selected working temperature of 550°, VIII and IX break down to the extent of *ca.* 50% (Table 10: VIII, runs 10,11; IX, runs 12,13), mainly by a new type of route involving scission within the acyl group and designated intra-acyl scission (I-A); considerable tar formation accompanies this reaction. There are also primary C^2 and other minor competitive primary routes as shown in the reaction scheme below. The weight contribution of competitive routes to the overall breakdown of VIII and (in parenthesis) of IX is estimated, and broken lines indicate the

most probable formation routes of tars, olefins and naphthalenes. Of the products shown, only the acyl-phenols were not conclusively identified. The scheme shows that, within limits of experimental error, the pyrolyses of VIII and IX are similar both qualitatively and semi-quantitatively.



Major I-A yields initially the alkyne CH:CR and phenyl formate (X). Little unchanged X remains in the pyrolysate; it is almost completely decarbonylated to phenol as previously observed by Adlokes et al.[31] The reaction scheme here therefore accounts for phenol, carbon monoxide,

acetylene and traces of X reported by Skraup and Nieten[74] in pyrolysis of VIII.

It is formally possible that VIII might yield the eventual I-A products, but not X, via a B^1 reaction:

$$CH_2{:}CH.COO.Ph \xrightarrow{?} [CH_2{:}C{:}CO] + PhOH \quad \ldots B^1$$

$$[CH_2{:}C{:}CO] \downarrow$$

$$CO + CH{:}CH \quad \ldots C^1$$

The intermediate methyleneketen and its possible isomerisation to propiolic aldehyde has already been discussed (p.33), and again in this case offers an acceptable route to carbon monoxide and acetylene. In the α-methyl-acrylate IX, however, a B^1 type reaction would involve the improbable migration of the α-methyl group to yield anisole, carbon monoxide and acetylene:

$$CH_2{:}CMe.COO.Ph \xrightarrow{?} [CH_2{:}C{:}CO] + PhOMe \quad \ldots B^1$$

$$[CH_2{:}C{:}CO] \downarrow$$

$$CO + CH{:}CH \quad \ldots C^1$$

Neither anisole nor acetylene was detected in the pyrolysate from IX and the observed products, phenol and methylacetylene, are best explained by an I-A reaction. The detection of X in the pyrolysates from both VIII and IX confirms this route. Since both esters yield I-A products in approximately equal amounts, it is not thought that in the pyrolysate from VIII these are to any extent attributable to the formally possible B^1.

Since X undergoes almost complete O[1], I-A should lead to equimolar yields of phenol, carbon monoxide and the alkyne OH OR. There was, in fact, invariably an alkyne deficiency well outwith experimental error, as is shown in Table 3.

Table 3- Pyrolysis of VIII and IX at 550°; molar yields of I-A products.

Run No.	10	11	12	13
Pyrolysand	VIII	VIII	IX	IX
Phenol, moles	0.14	0.11	0.07	0.07
Carbon monoxide, moles	0.08	0.06	0.08	0.08
Alkyne OH OR, moles	0.02	0.02	0.02	0.02

This deficiency is attributable to extensive secondary breakdown of the alkyne on the classical lines indicated by Berthelot[75], and is held to account for the heavy tar formation, the naphthalenes and (in part) the olefin traces. An analogous alkyne deficiency accompanied by heavy carbonisation has been observed in pyrolysis of phenyl vinyl ether[47]:

$$Ph.O.CH{:}CH_2 \longrightarrow PhOH + (OH{:}CH + Tars)$$

In Table 4 the approximate correlation between carbonisation and the extent of the I-A reaction in breakdown

of VIII supports this claim. As indicated in the reaction scheme, however, there must be some other tar-forming route, since it cannot all be accounted for by secondary alkyne pyrolysis.

VIII was pyrolysed in presence of certain free radical inhibitors (Table 10, runs 17-21). Thermally unstable compounds were necessarily avoided and the following inhibitors selected:

(i) hydroquinone,

(ii) phenanthraquinone,

(iii) 4-tert.-butylcatechol

(iv) benzoquinone,

and (v) copper.

Inhibitors (i)-(iv) were dissolved in the pyrolysand (1%); (v) was used as packing in the reactor. Table 4 compares the semi-quantitative breakdown of VIII itself and in presence of these inhibitors. The salient feature is the complete suppression of I-A by (i) and its partial suppression by (ii). Carbonisation in presence of (i) and (ii) is reduced. Overall breakdown in presence of (iv) and (v) is increased, mainly by an increase in carbonisation though the extent of I-A is unaltered. Polymer formation is also suppressed by (i), but σ^2 and the suspected R are not significantly affected by any of the chosen inhibitors.

Table 4 - Pyrolysis of VIII at 550°; effect of inhibitors (i)-(v)

Run no.	10-11*	17	18	19	20	21
Inhibitor	-	(i)	(ii)	(iii)	(iv)	(v)
Retention time, secs.	82	83	85	97	97	110
Gaseous pyrolysate, ml. at N.T.P./g. pyrolysand	40	20	70	90	110	170
Ester unchanged, %	49	91	74	63	33	22
Intra-acyl scission, %	28	-	9	15	28	29
Decarboxylation, %	7	7	3	9	11	10
Polymerisation, %	2	-	6	5	6	6
Carbonisation, %	15	2	8	8	22	33
Rearrangement	T	T	T	T	T	T

* - Figures represent the average of runs 10 and 11;

- - Nil; T - Trace.

It is concluded from this evidence that I-A is a free radical reaction. The following tentatively suggested sequence, applicable equally to VIII and IX, accounts for all the products attributed to the reaction and also (in part) for the observed olefin traces.

Initiation:

(1) $CH_2{:}CR.COO.Ph \longrightarrow CH_2{:}\dot{C}R + \dot{C}OO.Ph$

Propagation:

(2) $CH_2{:}\dot{C}R + CH_2{:}CR.COO.Ph \longrightarrow CH_2{:}CHR + \dot{C}H{:}CR.COO.Ph$

(3) $\dot{C}H{:}CR.COO.Ph \longrightarrow CH\ CR + \dot{C}OO.Ph$

(4) $\dot{C}OO.Ph + CH_2{:}CR.COO.Ph \longrightarrow H.COO.Ph + \dot{C}H{:}CR.COO.Ph$, etc.

$\downarrow$

CO+PhOH

The following steps may compete in propagation but cannot be exclusive since they do not explain the observed traces of X:

(5) $\dot{C}OO.Ph \longrightarrow CO + \dot{O}Ph$

(6) $\dot{O}Ph + CH_2{:}CR.COO.Ph \longrightarrow PhOH + \dot{C}H{:}CR.COO.Ph$, etc.

A similar sequence involving formation and breakdown of ethyl formate might formally account for the products attributed to the B[1] reaction in ethyl acrylate (IV):

$CH_2{:}CH.COO.Et \xrightarrow{?} CH{:}CH + H.COO.Et$ ...I-A

$\downarrow$

CO+EtOH ...θ^1

Since neither ethyl formate nor any products specific to its known breakdown[11] were detected in the pyrolysate,

I-A in IV may be discounted. This accords with the suggested free radical mechanism of the reaction; in the phenyl esters VIII and IX the postulated carbophenoxy radicals are stabilised by resonance in the aromatic ring, while in IV the corresponding carboethoxy radicals lack such stability and may be considered so unstable as to preclude the reaction.

The accelerating effect of (iv) and (v) on carbonisation, without increasing the extent of I-A, is difficult to explain. Carbonination may result from some complex free radical reaction catalysed by (iv) and (v); the participation of (v) in some pyrolytic reaction was indicated by a clear, copper-brown stain formed on the reactor surface. Treatment with mineral acids and heating in air at 500° did not remove the deposit and this particular reactor was not used again.

Like vinyl benzoate[25] (the structural isomer of phenyl acrylate) and other α-unsaturated esters[25,36,37], both VIII and IX undergo C^2, yielding a styrene CH_2:CRPh. Skraup and Mieten[74] did not record any C^2 products in pyrolysis of VIII and the detection of this route competing with I-A clarifies some earlier reports in the literature. Styrene traces detected by Filachione *et al.*[76,77] in pyrolysis of certain aryl α-acetoxypropionates can now be attributed to C^2 of aryl acrylates formed by primary A^1;

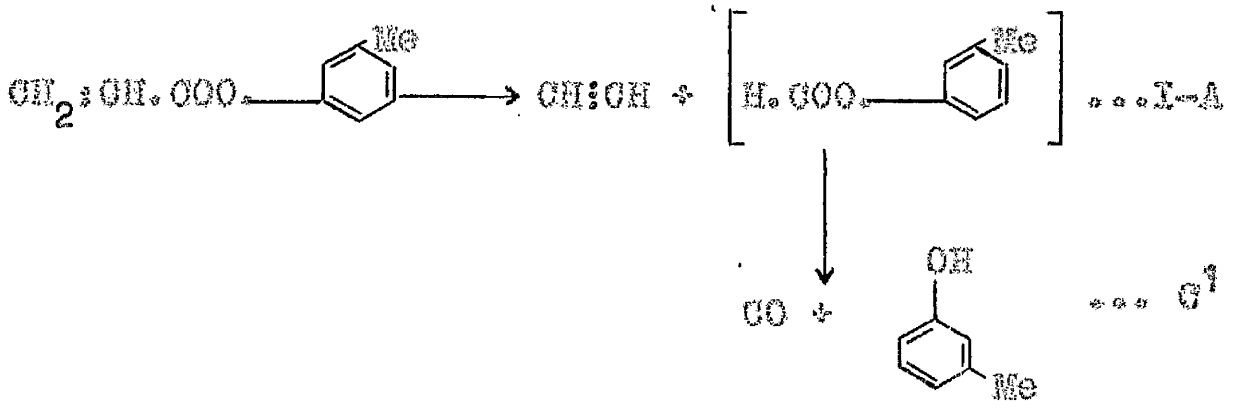
$$AcO.CHMe.COO.Ar \longrightarrow AcOH + CH_2{:}CH.COO.Ar \quad \ldots A^1$$

$$\downarrow$$

$$CO_2 + CH_2{:}CHAr \quad \ldots C^2$$

(Ar = Phenyl[76], 4-tert.-butylphenyl[77]).

Furthermore, when Ar = m-tolyl[77] the pyrolysate contained a little m-cresol which can be explained on the basis of an I-A reaction of m-tolyl acrylate:

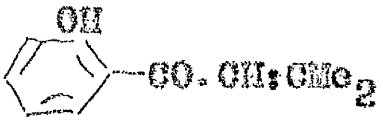


Although Table 4 shows the chosen inhibitors to have little significant effect on the extent of C^2 this does not necessarily mean that the reaction is not free radical, since such inhibitors are highly specific in their action.

The formation of a little polymerised ester almost certainly does not occur in the reactor packed section, where the temperature (550°) is beyond the probable ceiling limit. Polymerisation in some intermediate temperature zone between the packed section and the room temperature pyrolysate receiver is more likely.

There is a good precedent for the suspected acyl-phenols in the rearrangement of phenyl $\beta\beta$-dimethylacrylate

to o-ββ-dimethylacryloylphenol reported by Skroup and Beng[49]:

$Me_2C{:}CH.COO.Ph \longrightarrow$  ...R

The yield of 7% at 320-330° is increased to 17-25% by catalysis with hydrogen chloride traces.

Both VIII and IX yielded a small fraction showing phenolic colour reactions and forming a 2:4-dinitrophenyl hydrazone, which in its purest state also showed phenolic reactions. Infra-red spectrographic evidence supported the acyl-phenol structure, but conclusive micro-analyses could not be obtained from such small amounts.

To confirm the routes postulated for breakdown of VIII and IX in the foregoing reaction scheme, the following primary products were pyrolysed under similar working conditions:

Phenyl formate (X).

Only traces of X survived pyrolysis (Table 10, run 14), decomposition occurring exclusively by C^1 as in distillation of the ester[31].

Styrene (XI).

Badger and Buttery[78] have reported naphthalene in the

pyrolysis products of XI at 1000°. In the present work at 550° negligible breakdown of XI was observed (Table 10, run 15), so that its further breakdown cannot explain the naphthalene traces in the pyrolysate from VIII.

Grassie[7] reports the ceiling temperature of polystyrene to be ca.300°, so that polymerisation of XI is thought to occur at an intermediate temperature zone after the reactor packed section, as proposed above for polymerisation of VIII.

α-Methylstyrene (XII).

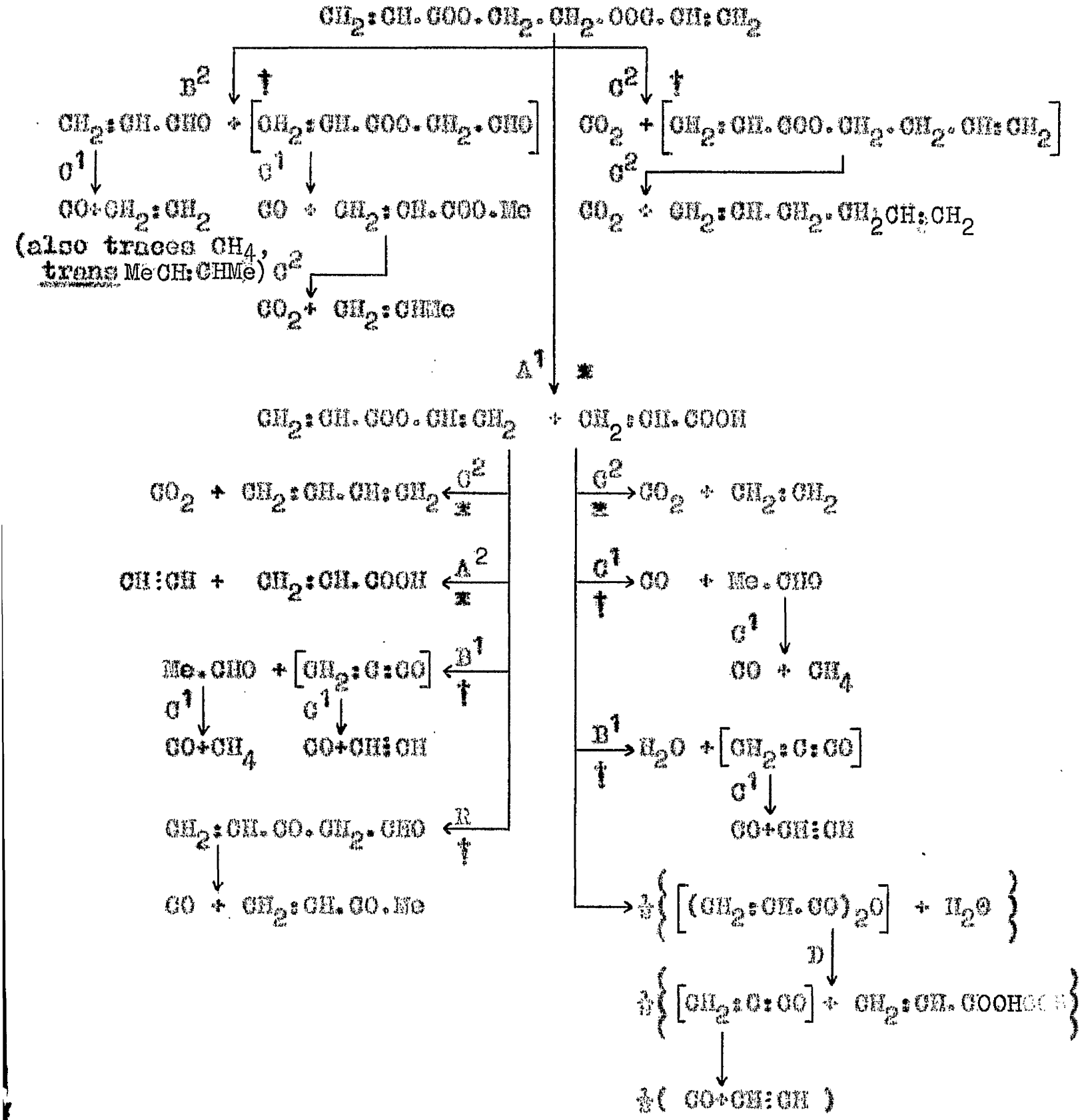
Similarly, 2:3-dimethylnaphthalene in the pyrolysate from the ester IX cannot be attributed to secondary breakdown of XII, which was found to survive unchanged apart from a little polymerisation (Table 10, run 16).

2.1.2. The pyrolysis of ethylene diacrylate and a related compound.

Ethylene diacrylate (XIII).

XIII represents two consecutive fumarate units in the polyester II. Investigation of its thermal degradation was unfortunately hindered by severe dermatitis caused by contact with the material.

From the work carried out it is estimated that in a Pyrex glass flow-reactor breakdown of XIII is negligible at 400°, ca.63% at 450° and ca.85% at 500° (Table 10, runs 22-25). Primary A^1, B^2 and C^2 routes were detected, but because of the complexity of the pyrolysate and the difficulties in handling it, cannot be estimated more accurately than as major (*) or minor (†) in the reaction scheme below. Competitive secondary and tertiary breakdown routes are similarly estimated, (T) signifying trace. All products except those in square brackets were identified, and though the scheme has not been conclusively proved to be complete, it is in accordance with the general routes of ester pyrolysis and is believed to show all but possibly some trace reactions.



The predictable A^1 scission predominates, yielding acrylic acid (V) and vinyl acrylate (XIV). Secondary

breakdown of V occurs as previously described (p.31) and certain products attributable only to further breakdown of XIV were detected.

It has been shown in pyrolysis of poly(ethylene terephthalate)[55] that carboxylic acid and vinyl ester end-groups formed by primary A^1 recombine to form an ethylidene linkage which then, in the classical manner of ethylidene di-acetate[48], undergoes complete disproportionation to acetaldehyde and an anhydride residue. Experiment showed that at ca.80° V and XIV react similarly, yielding acetaldehyde and acrylic anhydride (p.115):

$$CH_2{:}CH.COOH + CH_2{:}CH.COO.CH{:}CH_2 \longrightarrow \left[CH_2{:}CH.COO.\underset{\displaystyle Me}{CH}.OOC.CH{:}CH_2\right]$$

$$\downarrow$$

$$Me.CHO + (CH_2{:}CH.CO)_2O$$

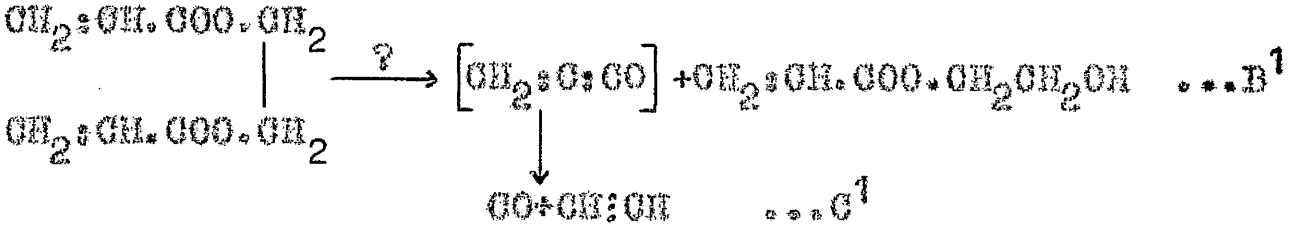
.....D

It is therefore thought probable that V and XIV react thus in pyrolysis of the diester XIII. Acetaldehyde was detected in the pyrolysate from XIII, but is not specific to this reaction. Acrylic anhydride was not detected; it is believed to undergo complete breakdown as postulated in pyrolysis of the acid V (p.31), reforming acrylic acid with acetylene and carbon monoxide as observed by Brown and Ritchie[66]. Since these products are also attributable to other routes, positive evidence of the recombination -

disproportionation sequence cannot be obtained.

Methane traces in the pyrolysate from XIII may be accounted for by a partial C^1 of acetaldehyde[30], and small amounts of acraldehyde (VI) by a minor primary B^2. This B^2 reaction should also yield acryloyloxyacetaldehyde, which was not detected in the pyrolysate. Not mentioned in the literature, it is reckoned to be an unstable compound which, though this is not the only formally possible reaction, yields the observed methyl acrylate (XVIII) by C^1 of the aldehyde group. The already described breakdown of VI (p.34) accounts in part for carbon monoxide, ethylene and methane traces, while propene is best attributed to C^2 of the α-unsaturated XVIII as is described below (p.56).

B^2 is the predictable acyl-oxygen scission in XIII, but the detection of competitive B^1 and B^2 in ethyl acrylate (IV) indicated the possibility of a B^1 in this case:



Other established routes yield carbon monoxide and acetylene from XIII. The specific B^1 product, 2-hydroxyethyl acrylate, was synthesised (p.115) but no corresponding compound was detected in the pyrolysate. If B^1 scission of

XIII does occur, it is therefore only to such a small extent that the product escapes detection.

The detection of hexa-1:5-diene shows successive primary and secondary C^2 of XIII to occur, though the primary product but-3-enyl acrylate was not isolated. C^2 of this α-unsaturated ester is predictable, as are the following A^1 and B^2 reactions:

$$CH_2{:}CH.COO.CH_2.CH_2.CH{:}CH_2 \begin{cases} \rightarrow CH_2{:}CH.COOH + CH_2{:}CH.CH_2.CH_2 \quad \ldots A^1 \\ \rightarrow CH_2{:}CH.CHO + \left[OHC.CH_2.CH{:}CH_2\right] \ldots B^2 \end{cases}$$

$$\downarrow$$

$$CO + MeCH{:}CH_2 \ldots C^1$$

If vinylacetaldehyde be presumed to undergo complete C^1, as is not unlikely, then these reactions do not yield any entirely specific products. It is therefore possible that these reactions do occur, and with C^2 result in the substantially complete breakdown of but-3-enyl acrylate. Confirmation of this claim by separate pyrolysis could not be obtained, since attempted preparations of the ester were invariably unsuccessful (p.115).

Pyrolysis of XIII yielded a trace solid aniline trap derivative (p.113) which did not correspond to the anilide of any known keten, nor to acrylanilide as the unstable

methyleneketen would formally yield:

$$CH_2{:}C{:}CO + PhNH_2 \xrightarrow{?} CH_2{:}CH.(CO).NHPh$$

The established routes of ester pyrolysis give no clue as to the nature of this unidentified derivative.

Secondary breakdown of XIV as shown in the reaction scheme was confirmed by a separate pyrolysis.

Vinyl acrylate (XIV).

Under similar working conditions but with a shorter retention time, XIV undergoes ca.57% decomposition (Table 10, run 26). Breakdown is in accordance with previously studied vinyl esters[25], though the extents of competitive routes vary. Major A^2 yields acrylic acid (V) and acetylene, and but-1:3-diene results from a major C^2. Acyl-oxygen scission, of the predictable B^1 type only, yields acetaldehyde and (via methyleneketen) carbon monoxide and acetylene. Products attributable to further breakdown of V (p.31) and methane by C^1 of acetaldehyde[30] were detected in the pyrolysate.

The most interesting route, and that yielding products specifically derived from XIV in the pyrolysate from the parent diester XIII, is a minor R to acryloylacetaldehyde. The intermediate keto-aldehyde in pyrolytic rearrangement of vinyl esters has not previously been detected[25], but in this case the high-boiling pyrolysate

residue yielded a 2:4-dinitrophenyl hydrazone which, though micro-analysis was not conclusive, corresponded best to that of acryloylacetaldehyde. This compound would be expected to be unstable under the pyrolysis conditions, and in fact its $O^{\dagger}$ product methyl vinyl ketone was detected.

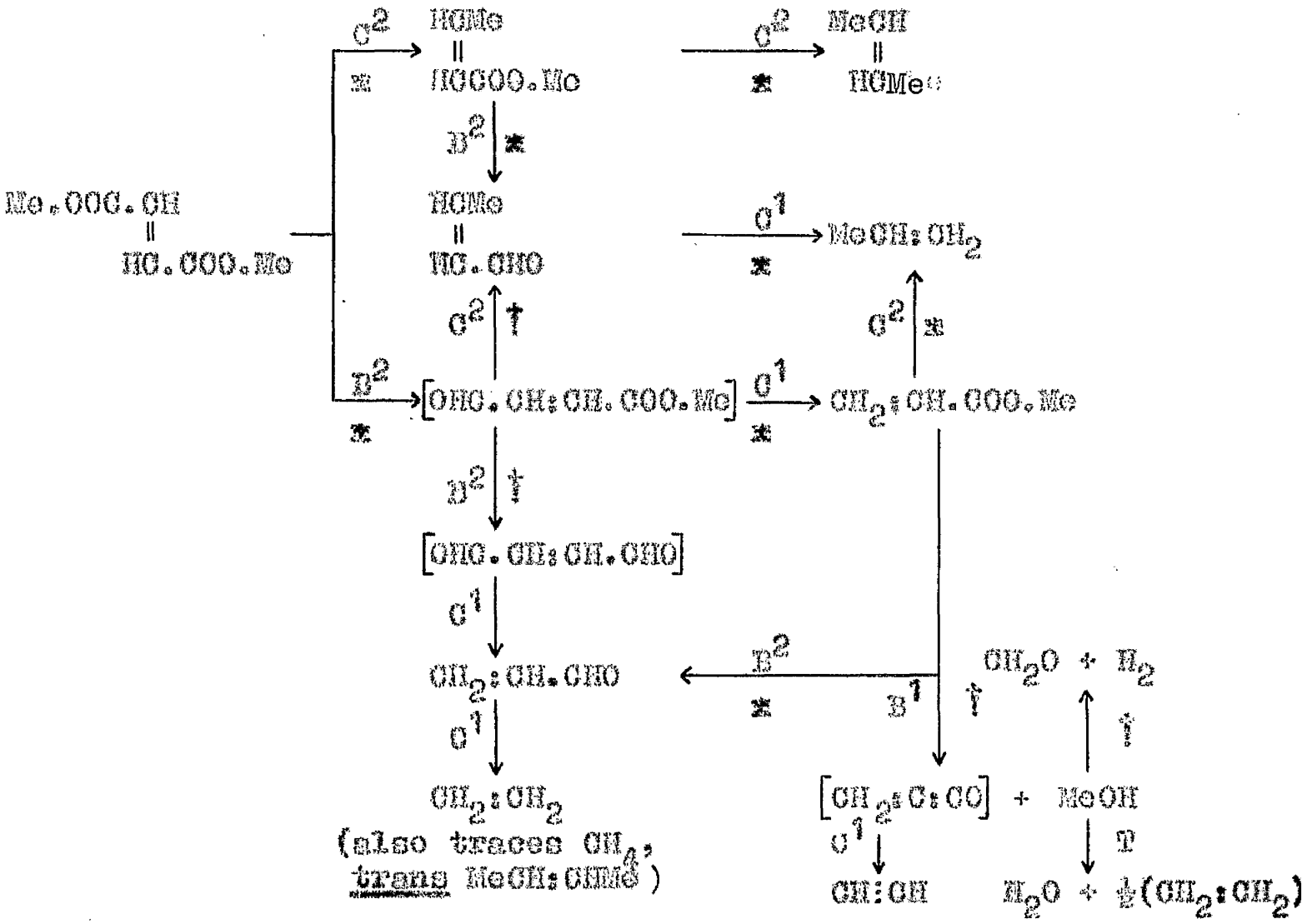
2.1.3. The pyrolysis of methyl fumarate and related compounds.

Methyl fumarate (XV).

In earlier work on model compounds representing segments of a maleic anhydride - ethylene glycol polyester, Forman[65] studied ethyl maleate. Since subsequent work[8,79,80] has shown this polyester to be substantially *trans* in structure, a fumarate was considered in the present study as a more realistic model compound. Methyl fumarate was chosen to preclude the overwhelmingly predominant A^1 encountered in ethyl esters; it represents two consecutive glycol units in the polyester II.

Pyrolysis of XV at 500° in a Pyrex glass flow-reactor results in *ca.* 40% decomposition (Table 10, run 27), by two major primary competitive routes, C^2 and B^2. Extensive secondary and tertiary breakdown complicates the reaction scheme below, in which the number of alternative routes to the same end-product restricts estimation of their extent to major (ǂ), minor (†) or trace (‡). Only those products

shown in square brackets were not identified; they are thought to be unstable. The scheme is believed to show the complete breakdown of XV. Carbon dioxide, formaldehyde and carbon monoxide liberated by C^2, B^2 and C^1 reactions respectively are omitted for simplicity. Hydrogen, attributable with an equal volume of carbon monoxide to partial C^1 of formaldehyde, is similarly omitted.



Major C^2 of XV (trans) yields methyl crotonate (XVI, cis), with no evidence for a trans product. XVI and

products attributable to its further breakdown were detected. The product accompanying formaldehyde in primary B^2, methyl β-aldehydoacrylate, was not isolated; it is not recorded in the literature and is thought to be completely unstable. Analysis of the pyrolysate indicates that in accordance with general pyrolysis routes its major breakdown is C^1 in the aldehyde group, yielding methyl acrylate (XVIII). This is the only apparent source of XVIII, a major product in the pyrolysate. Further breakdown of XVIII accounts in turn for other products as shown in the reaction scheme.

Semi-quantitative analysis of the pyrolysate also indicates a minor ester group C^2 of methyl β-aldehydoacrylate to crotonaldehyde (XVII), which is also attributable to a major B^2 of the ester XVI. Exclusive C^1 of XVII is responsible with a major C^2 of the ester XVIII for the observed propene. Though acraldehyde (VI) results mainly by a major B^2 of XVIII, it is also thought to derive <u>via</u> fumaric or maleic dialdehyde, which is formed from methyl β-aldehydoacrylate by a minor B^2. Like its immediate precursor, this dialdehyde is believed to be an unstable compound and was not detected. It is not recorded in the literature and would predictably undergo C^1 to VI.

No products corresponding to A^0 or B^1 reactions were detected.

VI has already been shown (p.34) to break down as in

the reaction scheme. The following separate pyrolyses under similar conditions confirmed the postulated breakdown of XVI, XVII and XVIII.

Methyl crotonate (XVI).

Major C^2 and E^2 reactions comprise an overall breakdown of ca.23% in XVI. C^2 yields trans-but-2-ene, with no evidence for a cis product in the pyrolysate of XVI or XV. A major E^2 of XVI to crotonaldehyde (XVII) is thought to account for the major part of XVII in the pyrolysate from XVI, that arising via methyl β-aldehydoacrylate being of little account. By analogy with ethyl acrylate (IV, p.29), XVI might be expected to undergo a E^1 to methanol and, via ethylideneketen, carbon monoxide and methylacetylene or its isomer allene:

$$\text{MeCH:CH.COO.Me} \xrightarrow{?} [\text{MeCH:C:CO}] + \text{MeOH} \quad \ldots E^1$$

$$[\text{MeCH:C:CO}] \rightarrow \text{CO} + \text{MeC:CH} \quad \ldots C^1$$

$$\text{MeC:CH} \rightleftarrows \text{CH}_2\text{:C:CH}_2 \quad \ldots R$$

Methanol was detected in the pyrolysate from the fumarate XV but not from the crotonate XVI, and neither ester yielded methylacetylene or allene. Hence, it is concluded that E^1 does not occur in breakdown of XVI and that some other route (p.56) is responsible for the methanol in the pyrolysate from XV.

Crotonaldehyde (XVII).

Decomposition of XVII occurs to the extent of ca.35% (Table 10, runs 29,30), exclusively by G^1 to propene. The olefin deficiency observed in breakdown of acraldehyde (VI, p.34) and subsequently by Forman[65] in pyrolysis of α-methylacraldehyde, isomeric with XVII, was in this case of negligible extent. Since both XVII and α-methylacraldehyde decarbonylate to the same olefin, propene, this supports the earlier claim that the olefin deficiency in pyrolysis of VI results from a primary reaction of the aldehyde rather than from secondary pyrolysis of ethylene.

Methyl acrylate (XVIII).

Major E^2 and G^2 in XVIII, yielding respectively acraldehyde (VI), by elimination of formaldehyde, and propene, account for almost all of the ca.50% total breakdown (Table 10, runs 31-33). This E^2 is the main source of VI in the pyrolysate from XV, little being formed via the postulated methyl β-aldehydoacrylate. It is difficult to estimate the respective contributions of G^2 in XVIII and G^1 in the aldehyde XVII to the propene yield from the ester XV; both are major reactions.

Pyrolysis of XVIII yields methanol, carbon monoxide and acetylene by a minor E^1, thereby explaining the methanol in the pyrolysate from XV. The fact that this reaction

should occur in the acrylate XVIII but not in the crotonate XVI, which differs only in having a β-methyl substituent, may indicate that the unknown mechanism of E^1 is precluded in XVI by the electron-repelling influence of the methyl group.

It has been shown[31] that the major breakdown of methanol is dehydrogenation to formaldehyde. XV and XVIII yielded products in accordance with this reaction, and also traces of water which are attributable with ethylene (in part) to a minor dehydration of methanol as reported by Bone and Smith[30].

Methyl maleate was pyrolysed to indicate the effect of the cis structure on breakdown.

Methyl maleate (XIX).

In the conditions used in pyrolysis of the trans ester XV, XIX was found as expected to be much less stable, only ca.5% surviving unchanged (Table 10, runs 34,35). The pyrolysate contained a weight of XV corresponding to a ca.60% isomerisation of maleate to fumarate, assuming ca.40% breakdown of XV as already estimated. There is thus ca.35% breakdown of XIX to smaller scission products. The nature of the primary and subsequent scission routes and their approximate contribution to this total are identical, within

experimental limits, to the breakdown of XV as shown in the foregoing reaction scheme.

It is predictable that the major pyrolytic reaction of XIX should be conversion to the isomer of lower energy content, as occurs also in pyrolysis of dibenzyl maleate[30]. Meerwein and Weber[32] have recorded isomerisation of XIX to XV in presence of potassium, which they claim activates the double bond. More striking is the fact that both maleate and fumarate on C^2 yield exclusively the cis ester, methyl crotonate, which in turn yields exclusively trans-but-2-ene on C^2 and crotonaldehyde (cis) on B^2. It is apparent from this that on pyrolytic production of a compound which can exist as two geometric isomers, thermal activation of the double bond results in the exclusive formation of the more stable isomer, no matter what the isomeric form of the parent molecule.

2.1.4. The pyrolysis of poly(ethylene fumarate) and related compounds.

Poly(ethylene fumarate) (II).

From the foregoing work on model compounds IV, XIII and XV it is predictable that the major scission routes in breakdown of II are A^1 and C^2. The possible occurrence of B^2 and, to a lesser extent, of B^1 is also indicated.

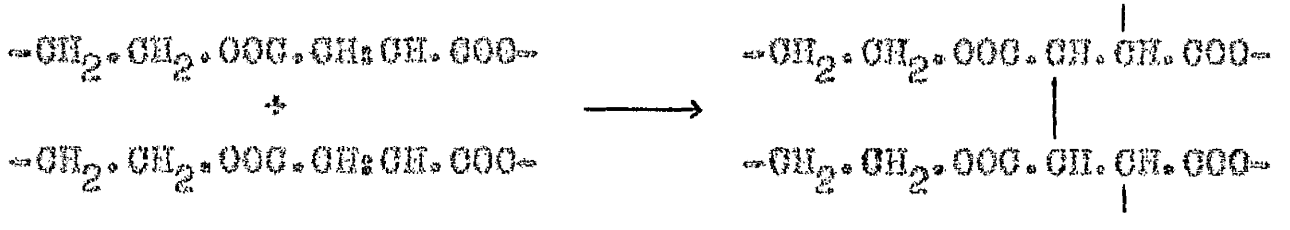
It has now been found that in fact II undergoes pyrolysis by three major primary competitive routes:

(1) further linear polycondensation, followed by cross-linkage and eventual carbonisation,

(2) A^1, yielding chain fragments and low molecular weight products, and

(3) C^2, yielding a non-fumarate polyester.

Initial experiments in a static reactor (Table 18, runs 42-45) showed condensation followed by cross-linkage and then carbonisation to occur before scission products of any type were detected. Linear increase of chain length is not unexpected, since II of low DP_n (number average degree of polymerisation) was normally used in an effort to simplify analysis of the pyrolysate. Figure 2 shows the increase of DP_n against time at 250°; the initial value of 5.4 increases to 16.3 after 30 minutes and to 48.4 after 60 minutes. Complete insolubility within 75 minutes is attributed to cross-linkage through the fumarate double bonds:



Further heating at 250° results in carbonisation, while at 300° cross-linkage and carbonisation occur within 10 minutes.

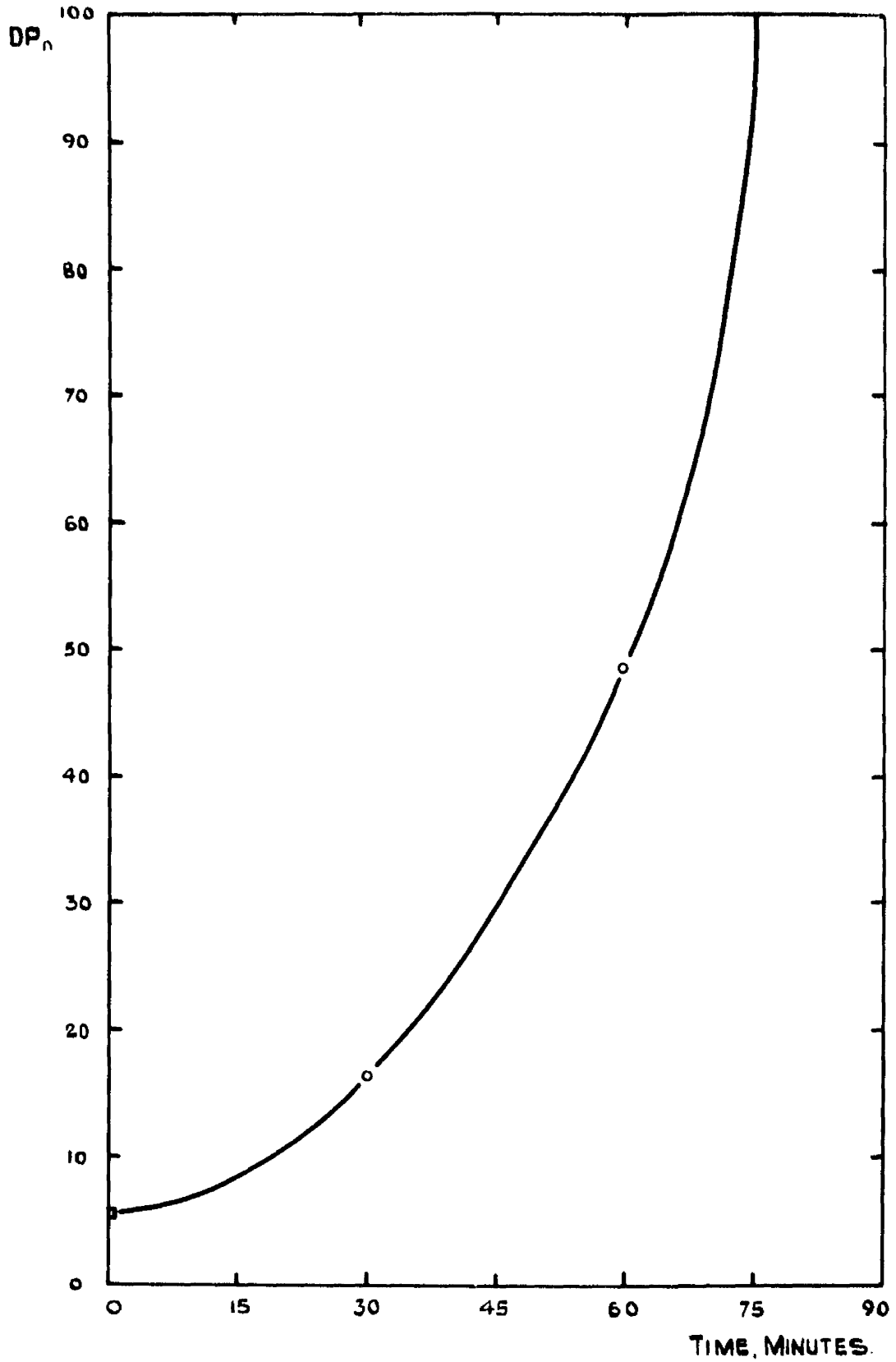
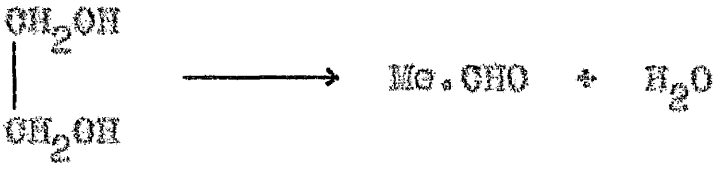


FIG. 2- INCREASE IN DP$_n$ OF POLY (ETHYLENE FUMARATE) AT 250°

Since it has been observed by Vincent[3] and in this work (p.99) that II cross-links on heating in presence of oxygen, these experiments were carried out under nitrogen and carbon dioxide rigorously purified of oxygen traces. There is no doubt that cross-linkage may be achieved thermally without any catalyst.

In flow pyrolysis of II at 400° (Table 10, runs 37-40), these reactions yielding macromolecules accounted for ca.50% of the pyrolysand weight as carbonised material retained in and eventually blocking the reactor. The presence of water as a major low molecular weight product is adequate proof of further linear polycondensation. It cannot all be accounted for by that originally present in the slightly hydroscopic[83] polyester, nor by any of the observed breakdown routes. Residual unreacted ethylene glycol might formally dehydrate to the observed acetaldehyde:



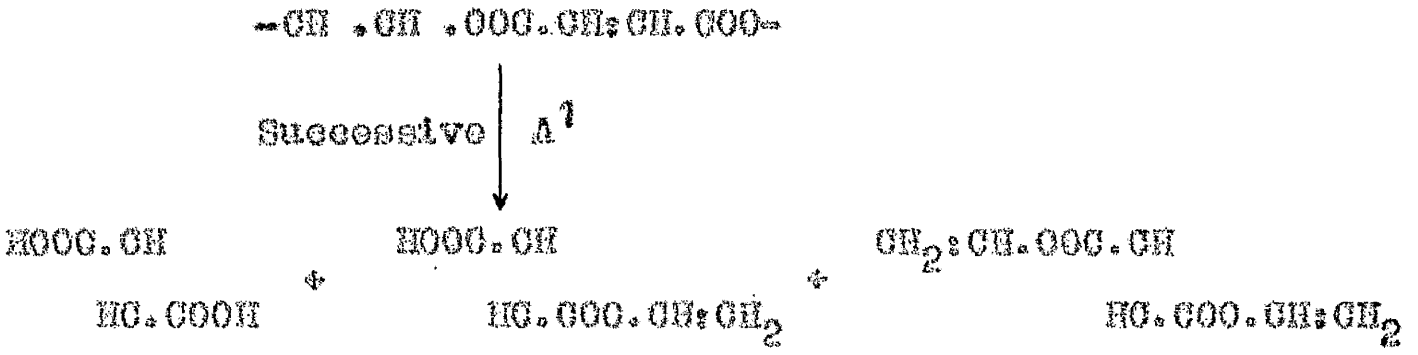
Ethylene glycol has, however, been shown[84] to be stable at 400° and in any case the pyrolysate contained no unreacted glycol, which is probably almost completely removed by the purification methods employed (p. 99). Acetaldehyde can be otherwise explained and hence water is best attributed to further polycondensation.

Under flow pyrolysis conditions, where higher temperatures were employed, macromolecule formation is countered by A^1. The products of this reaction can be explained equally well by its occurrence in linear II or in residual polyfumarate segments between cross-links. A^1 yields primarily carboxylic acid (a, below) and vinyl ester end-group fragments (b, below).

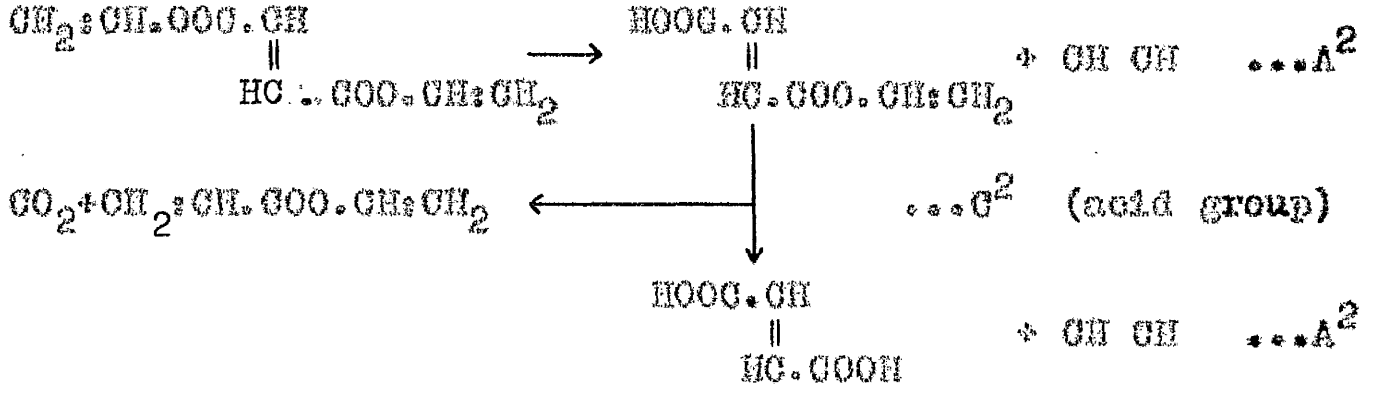
$$\sim CH{:}CH.COO.CH_2.CH_2.OOC\sim \longrightarrow \underset{a}{\sim CH{:}CH.COOH} + \underset{b}{CH_2{:}CH.OOC\sim} \quad \ldots A^1$$

In a preliminary run at 350° in an unpacked flow-reactor (Table 10, run 36) both a and b end-groups were identified. The pyrolysate consisted essentially of II with altered end-groups, including carboxylic acid and vinyl ester, and had $\overline{DP}_n$ ca.3 compared to the pyrolysand value of ca.6.4 . It is probable that under these conditions a state of simultaneous condensation (in which a may participate) and A^1 exists.

The pyrolysate emerging from the reactor at 400° did not contain a and b but products attributable to their further breakdown. Successive A^1 reactions at each ester residue in II and its subsequent fragments would eventually yield products comprising essentially fumaric acid (XX), monovinyl fumarate and divinyl fumarate:



XX in appreciable quantity, but neither ester, was detected in the pyrolysate from II. It is held that these multiple-unsaturated esters are unstable in the working conditions, and that they account for the observed products vinyl acrylate (XIV) and (in part) XX, carbon dioxide and acetylene by decomposing as follows in accordance with general ester pyrolysis routes:



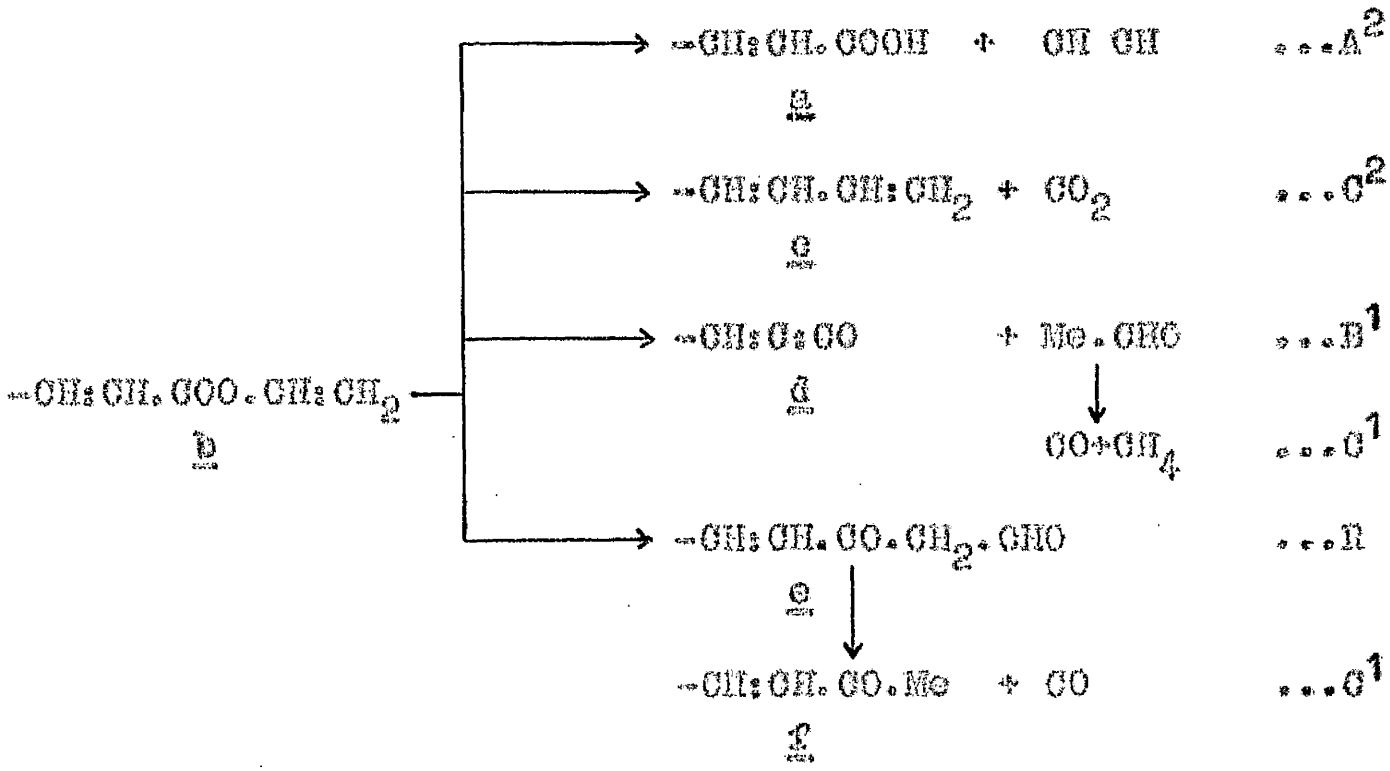
There are other formally possible breakdown routes, but since products specifically attributable to them were not detected they can at most be of only minor extent. XIV is the only observed product peculiar to the breakdown of mono- and di-vinyl fumarate. The well-established[14] ease of carboxylic acid C^2 explains the formation of XIV from the monoester in preference to reactions involving the ester group.

Though specific pyrolysis products of XIV were not detected in the pyrolysate from II, it may yield acrylic acid (V) and acetylene by A^2. Since, however, the acid XX is a primary A^1 product and is present in greater quantity, the observed V is thought to be formed mainly by C^2 of this dibasic acid. Separate pyrolysis of XX (Table 10, run 41) established this as the exclusive breakdown route:

$$\begin{matrix} HOOC.CH \\ \| \\ HC.COOH \end{matrix} \longrightarrow CH_2{:}CH.COOH + CO_2 \qquad \ldots C^2$$

Only small amounts of V were detected; it is thought to undergo appreciable C^2 as has been established as its major breakdown route (p.31), thus accounting for ethylene in the pyrolysate from II.

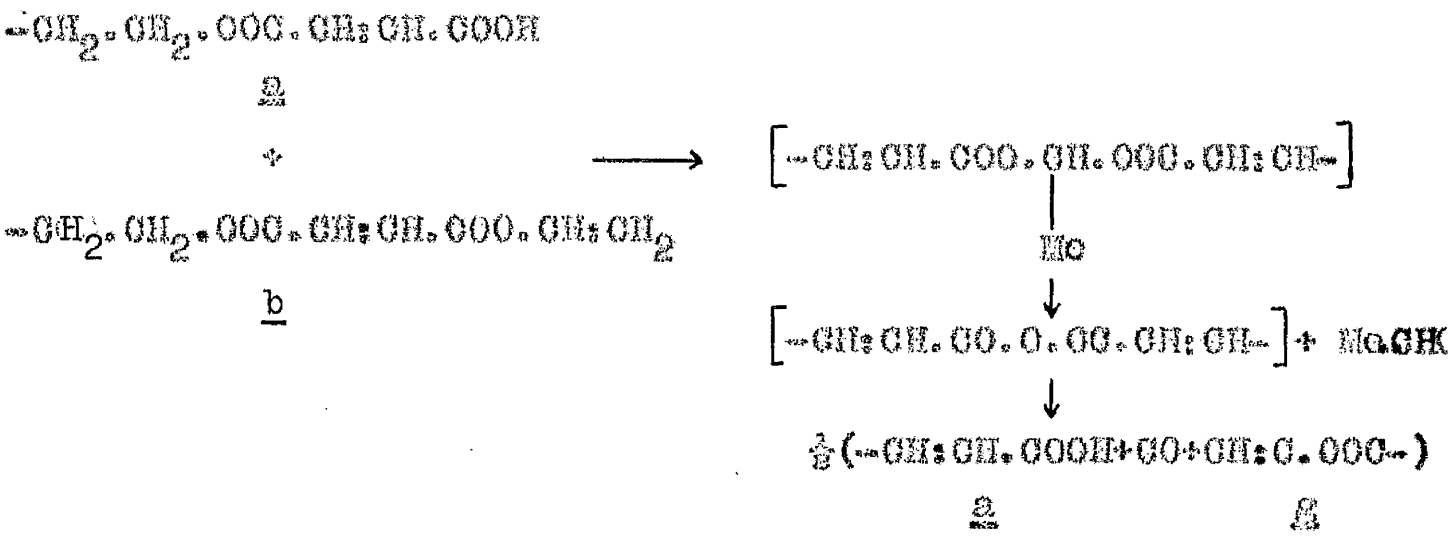
Fragments a and b are likely to undergo breakdown involving their end-groups. Small amounts of carbon dioxide are doubtless attributable to end-group C^2 of a in addition to the reactions shown above, while the pyrolysis of XIV (p.51) indicates probable end-group degradation of b thus:



This breakdown is the probable origin (in part at least) of the products carbon monoxide, acetaldehyde, methane traces and acetylene. The polymer fragments c, d, e and f were not detected; even if their end-groups are presumed to be stable, which in the case of d and e especially is unlikely, their detection in the complex pyrolysate would be difficult.

By analogy with the pyrolysis of poly(ethylene terephthalate)[60], a and b might yield acetaldehyde and an anhydride grouping by recombination and disproportionation. Acrylic acid (V) and vinyl acrylate (XIV), which may be considered as models representing a and b respectively, have been shown to undergo a similar reaction, and the possibility of its occurrence in the pyrolysis of ethylene diacrylate (XIII) has been discussed (p.48). The considerable quantities of

acetaldehyde in the pyrolysate from II suggests that it may originate in part from this reaction, the anhydride grouping escaping detection by decomposing in the manner of acrylic anhydride:



There is little prospect of confirming this reaction by identification of the propiolic ester end-group fragment f, which is almost certainly unstable.

In regard to A[1] II shows certain similarities to poly(ethylene terephthalate), but its overall pyrolysis invariably yields much more carbon dioxide. This is attributed to the ease of primary C[2] in the olefinic α-unsaturated polyester, the reaction causing the complete disruption of the fumarate structure at 400°. At this temperature, flow pyrolysis yields a thermoplastic material, soluble in common organic solvents, and shown by infra-red spectrometry (Fig.3) to be an ester but not a fumarate. The characteristic fumarate absorption peak at 975 cm.$^{-1}$ is absent and the

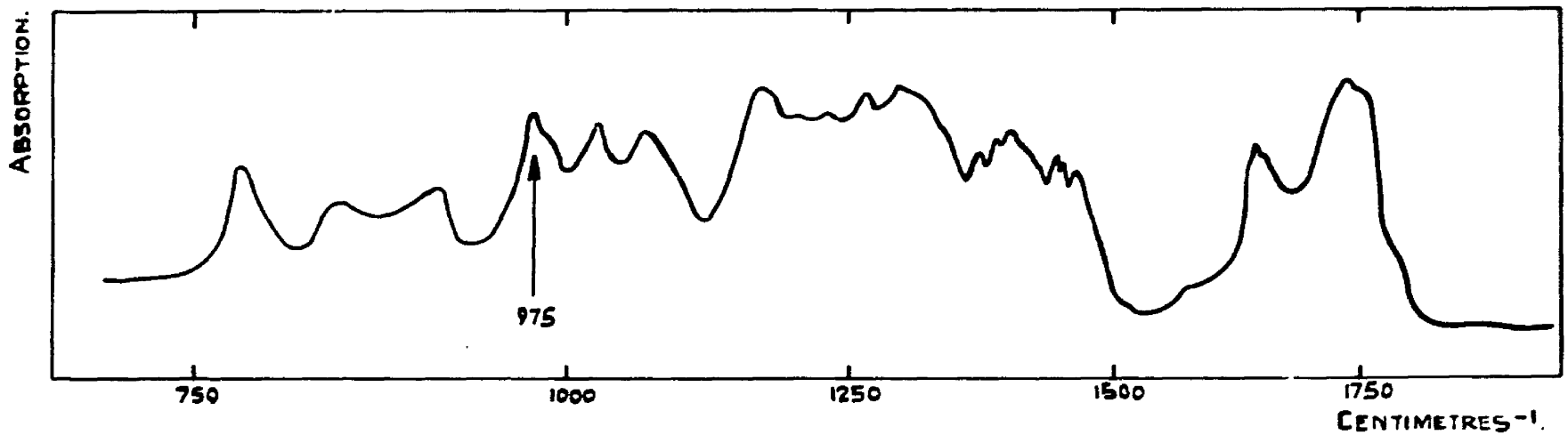


FIG. 3a - INFRA-RED ABSORPTION SPECTRUM OF POLY (ETHYLENE FUMARATE.)

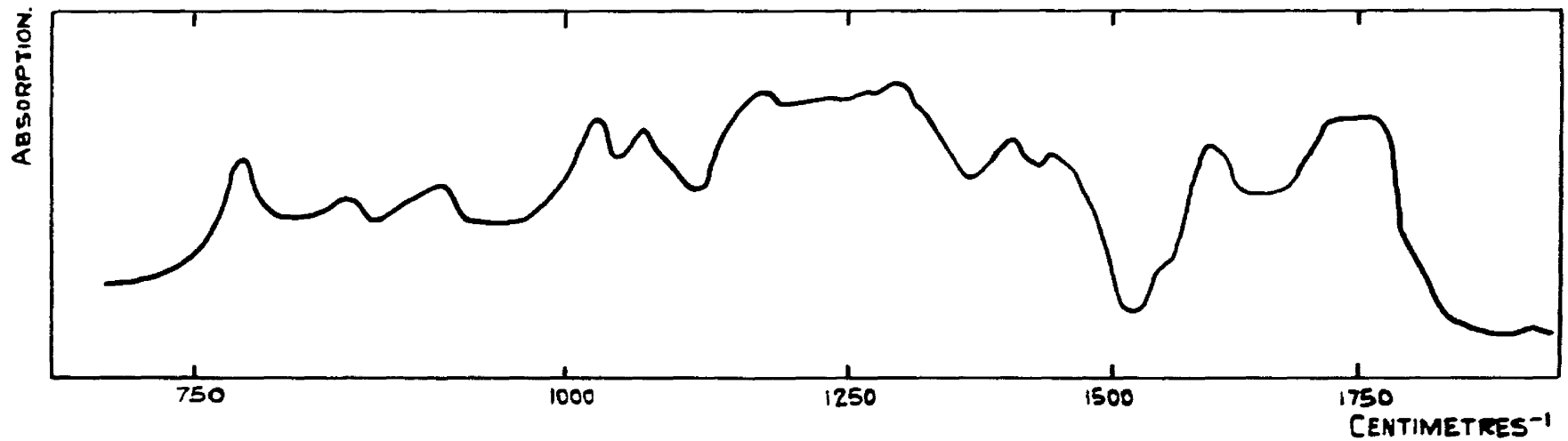


FIG. 3b - INFRA-RED ABSORPTION SPECTRUM OF POLYESTER OBTAINED IN PYROLYSIS OF POLY (ETHYLENE FUMARATE.)

spectrum altered in the region of the carbonyl frequency.

From the analytical evidence, this product is a linear polyester. Since it is linear the non-fumarate structure does not derive from saturation by cross-linking, which is unlikely in any case to saturate every fumarate double bond. The formation of this polyester is best attributed to primary internal C^2 of II. This reaction does not occur by stepwise elimination of successive carboxyl groups along the chain, since any residual ester linkages would then retain the fumarate structure. It is conceivable, however, that in a fumarate ester one carboxyl group enhances the influence of α-unsaturation on C^2 of the other. Elimination of one carboxyl group would hence leave an ester linkage more stable towards C^2 than residual unchanged fumarate units. Thus, it might be predicted that primary internal C^2 would eventually eliminate every second carboxyl group from II:

$$\text{-}CH_2\cdot CH_2\cdot OOC\cdot CH{:}CH\cdot COO\cdot CH_2\cdot CH_2\cdot OOC\cdot CH{:}CH\cdot COO\text{-}$$

$$\downarrow \text{-}CO_2$$

$$\text{-}CH_2\cdot CH_2\cdot CH{:}CH\cdot COO\cdot CH_2\cdot CH_2\cdot OOC\cdot CH{:}CH\cdot COO\text{-} \quad \ldots C^2$$

$$\downarrow \text{-}CO_2$$

$$\text{-}CH_2\cdot CH_2\cdot CH{:}CH\cdot COO\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot COO\text{-} \quad \ldots C^2$$

This idealised polyester would on hydrolysis yield β-2-hydroxyethylacrylic acid;

$$\text{-}CH_2\cdot CH_2\cdot CH{:}CH\cdot COO\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot COO\text{-} \xrightarrow{\text{Hydrolysis}} HOCH_2\cdot CH_2\cdot CH{:}CH\cdot COOH$$

Hydrolysis of the actual polyester yielded in fact a low molecular weight liquid acid product (with no evidence for fumaric acid) which could not be characterised. However, either carboxyl group from residual fumarate units might be eliminated and the resulting polyester quite irregular, yielding a complex hydrolysate.

The three reactions described here have been established as the major breakdown routes of II at 400°. It is not claimed, however, that there are no other routes, since products of minor reactions might well escape detection.

Two polyesters in which A^1 is precluded were prepared and pyrolysed for comparison of their thermal stability with that of II.

Poly(neo-pentylene fumarate) (XXI) and poly(p-phenylene fumarate) (XXII).

XXI lacks a ß-hydrogen atom while in XXII it is firmly bound in the aromatic ring. These polyesters and II were pyrolysed under similar static conditions (Table 19, runs 46-48). No effort was made to analyse liquid or solid products. Instead, the easily estimated and analysed gas yields were compared, and were found to decrease in the order II (55 ml./g.), XXI (34 ml./g.) and XXII (30 ml./g.). In many pyrolytic reactions the liberated gas volume is

proportional to the extent of overall breakdown, though this relationship is not invariable. It appears likely from the results that both XXI and XXII are more thermostable than II.

2.1.5. The pyrolysis of poly(ethylene fumarate - methyl α-methylacrylate) and related compounds.

Poly(ethylene fumarate - methyl α-methylacrylate) (I).

In pyrolysis of I it has been found that the initial reaction is liberation of monomeric methyl α-methylacrylate. There is evidence that this reaction, presumed to be free radical and initiated at unsaturated methylacrylate chain ends as in degradation of poly(methyl α-methylacrylate) (III) itself[7], is terminated at the inclusion of a fumarate cross-linking unit.

In static pyrolysis of I at 200° and 250° (Table 20, runs 49, 53) methyl α-methylacrylate and traces of water were detected, but not any scission products as described in breakdown of II. It is therefore clear that breakdown in the fumarate residues requires a higher temperature than does depolymerisation of the methylacrylate chains. The observed water may have been originally present in II or may result from condensation of fumarate chain end-groups, though this is less likely in the resin than in the more mobile linear polyester.

Only small amounts of methyl α-methylacrylate were liberated. Since Grassie's work[7] indicates that appreciable depolymerisation might be expected at the working temperatures, I was compared with the following related polymers under similar static pyrolysis conditions.

poly(methyl α-methylacrylate)(III), poly(methyl fumarate - methyl α-methylacrylate)(XXIII) and poly(neo-pentylene fumarate - methyl α-methylacrylate)(XXIV).

I yielded traces of methyl α-methylacrylate over 60 minutes at 200° and 11% over 120 minutes at 250°; a corresponding weight of III (on the basis of approximate α-methylacrylate in I) yielded respectively 6% and 28% under these conditions (Table 20; I, runs 49,53; III, runs 50, 54). To confirm that the lower monomer yield from I is not simply apparent, because of slower diffusion out of the cross-linked molecule, the linear copolymer XXIII was pyrolysed. In XXIII, each methyl fumarate unit represents a cross-linking unit in the resin I. Since a corresponding weight of XXIII showed a similar though less marked reduction in monomer yield (Table 10, runs 51,55), it is concluded that diffusion does not entirely account for the reduced yield from I. It is believed that in both I and XXIII the free radical depolymerisation is terminated at the inclusion of a fumarate unit. This accords with Grassie's findings[7] in

methyl α-methylacrylate - acrylonitrile copolymers, in which, however, depolymerisation is preceded by chain scission in the region of the acrylonitrile units and thereafter terminated at these units (p.27). Scission preceding depolymerisation in the resin I is therefore a possibility, but would be extremely difficult to detect because of the insolubility of I.

The resin XXIV also showed a lower monomer evolution than did III (Table 20, runs 52,56). The corresponding resin of poly(p-phenylene fumarate) could not be compared; the linear polyester (XXII) did not copolymerise with methyl α-methylacrylate owing, it is thought, to the difficulties in removing unreacted inhibiting hydroquinone from XXII.

The exact composition of the copolymers I, XXIII and XXIV cannot be calculated without knowing the monomer reactivity ratios of methyl α-methylacrylate in relationship to II, XV and XXI. This, however, does not fundamentally affect the comparison of monomer yield from each with that from a reasonably corresponding weight of III.

2.2. Threshold Temperature Determination.

The pyrolysends listed in Table 2 are considered in this section. The apparatus is described in section 3.1.3., and experimental results are given in Tables throughout the

text.

2.2.1. Concept of threshold temperature.

It is now well known that most organic esters pyrolyse by two or more competitive routes (p.4). The proportional contribution of these routes to the overall breakdown has frequently been estimated but no attempt has hitherto been made to compare their onset or threshold temperatures. An absolute value of this temperature cannot be conceived; variable conditions such as retention time, nature of the reactor and packing material, contact surface area and pressure, etc., must always be considered. Fisher et al.[65] have shown quantitative variations in pyrolysis of methyl acetoxypropionate with varying reactors and packing materials, where retention time, contact volume and surface area also vary. Carbonised deposits have been found to catalyse isomerisation[10] and pyrolysis at reduced pressure to limit secondary breakdown and tar formation (Kraft[16]).

In the present work an apparatus has been devised whereby threshold temperatures of pyrolytic routes can be compared with all other influencing conditions remaining constant. It depends essentially upon detection of gaseous products in a photo-cell system, and affords comparison not only of competitive routes in one compound but also of corresponding routes in different pyrolysands. Pohl[58] has

previously described a constant temperature system in which the extent of breakdown is followed by measurement of the gaseous pyrolysate volume. This allows a comparison of retention times rather than threshold temperatures and it is thought that the results obtainable from the present apparatus are of more practical value in this study.

2.2.2. Threshold temperature determination in model compounds.

Ethyl fumarate (XXV) was selected to represent residual unsaturated polyester units in I and ethyl maleate (XXVI) to compare the stability of the cis and trans isomers. Points of cross-linkage in I are represented by ethyl succinate (XXVII) and commercially incorporated saturated polyester residues by ethyl adipate (XXVIII) and ethyl sebacate (XXIX).

The occurrence of primary competitive A^1 and C^2 in pyrolysis of XXV, XXVI and XXVII has been indicated[36]; Brown and Ritchie[66] have shown XXVIII and XXIX to undergo primary A^1 but not primary C^2. The threshold temperatures of liberation of ethylene, $T(CH_2{:}CH_2)$, and carbon dioxide, $T(CO_2)$, from these primary A^1 and C^2 reactions respectively are listed in Table 5.

The following salient points emerge from the results:

(1) There is little difference in $T(CH_2{:}CH_2)$ values for XXV and XXVI, but in XXVI $T(CO_2)$ is much higher.

Table 5 - Threshold temperatures in XXV, XXVI, XXVII, XXVIII and XXIX.

Pyrolysand (0.01 moles)	$T(CO_2)$	$T(CH_2:CH_2)$
XXV	370	340
XXVI	315	350
XXVII	*	330
XXVIII	*	310
XXIX	*	320

* - Primary C^2 does not occur[66].

This suggests that the C^2 reaction in the polyester II may be facilitated by the trans structure.

(2) Comparison of $T(CH_2:CH_2)$ and $T(CO_2)$ values for XXV indicates that in II A^1 should occur at a lower temperature than C^2.

(3) Since $T(CH_2:CH_2)$ is slightly lower for XXVII than for XXV, A^1 in I may occur preferentially at points of cross-linkage.

(4) The comparatively lower values of $T(CH_2:CH_2)$ in XXVIII and XXIX suggests that the commercially included saturated ester residues are more susceptible to A^1 than unsaturated fumarate units.

(5) There is no regular correlation between T(CH_2:CH_2) and the number of methylene groups in XXVII, XXVIII and XXIX.

2.2.3. Threshold temperature determination in poly(ethylene fumarate) and related compounds.

Qualitative pyrolysis of II (Section 2.1.4.) has shown that carbon dioxide from primary internal C^2 and ethylene, acetylene traces and acetaldehyde via primary Δ^1 are among the major scission products. Threshold temperatures of liberation of these products are listed in Table 6. Experiments on the removal of acetylene to permit detection of ethylene alone were not completely successful (p.91), and the threshold temperature of these two gases together is given as T(unsats.).

Table 6 - Threshold temperatures in II, XXI, XXII and XXX.

Pyrolysend (0.01 moles)	T(CO_2)	T(unsats.)	T(Me.CHO)
II (DP_n ca. 3-9)	295	305	305
II (i) - (iii) (vi) - (viii)	295	305	305
XXI	290	335	290
XXII	280	*	*
XXX	345	320	330

* - Unsaturated gases and acetaldehyde not liberated below 500°.

(i), etc. - Inhibitors.

Table 6 shows that in II $T(CO_2)$ is lower than T(unsats.) or T(Me.CHO), indicating C^2 to occur at a lower temperature than A^1. This contrasts with the corresponding values in the model compound XXV, but accords with the postulated primary internal nature of C^2 in the polyester. It is held that this reaction liberates carbon dioxide in quantity before it is formed with ethylene, acetylene, acetaldehyde and other products by reactions involving the A^1 fragments g and h.

The determined threshold temperatures are seen to be independent of chain length in II within the approximate DP_n limits 3-9. Nor was any variation observed in the values when the following free radical inhibitors were dissolved in the pyrolysand:

(i) 1% hydroquinone,

(ii) 1% phenanthraquinone,

(iii) 1% 4-tert.-butylcatechol,

(vi) 10% hydroquinone,

(vii) 1% o-phenylenediamine

and (viii) 5% benzaldehyde.

A^1 is now quite generally accepted as a molecular reaction[22] and no alteration in T(unsats.) or T(Me.CHO) values is expected. The free radical nature of C^2, however, has already been suggested (p.19) and the constancy of $T(CO_2)$ may simply result from the fact that none of the somewhat

arbitrarily chosen inhibitors is specific for the reaction.

Threshold temperatures for poly(neo-pentylene fumarate)(XXI) and poly(p-phenylene fumarate)(XXII) are also listed in Table 6. The values confirm only in part the results of Section 2.1.4. indicating these polyesters, in which lack of an available β-hydrogen atom precludes A^1, to have a greater thermal stability than II. XXII yields no ethylene, acetylene or acetaldehyde below 500°. XXI does yield these products, T(unsats.) being greater than in II though T(Me.CHO) is unaltered. Unsaturated gases and acetaldehyde from XXI must be formed by some reaction other than A^1 and not pursued in this work. $T(CO_2)$ varies little between II and XXI but is rather lower in XXII. This agrees with the primary internal nature of C^2, since in II and XXI the degree of α-unsaturation is equal but in XXI is enhanced by the aromatic nucleus so that the reaction might predictably occur more readily. Phenyl acrylate (VIII), which can be regarded as a model for XXII, has been shown to undergo appreciable C^2 (Section 2.1.1.).

Again in Table 6, $T(CO_2)$ of the saturated poly(ethylene succinate) (XXX) is higher than T(unsats.) or T(Me.CHO), in contrast to the α-unsaturated polyesters II, XXI and XXII where the reverse is true. Further proof of the primary internal nature of C^2 is furnished by this: only in the saturated XXX is carbon dioxide elimination following primary A^1 not preceded by primary internal C^2. Unsaturated

gases and acetaldehyde from XXX are also attributable to predictable reactions following A[1].

2.2.4. Threshold temperature determination in poly(ethylene fumarate - methyl α-methylacrylate) and related compounds.

Threshold temperatures of the resins Ia, Ib and Ic, prepared using 0.1, 0.2 and 0.5 mole % benzoyl peroxide catalyst respectively, are shown in Table 7.

Table 7 - Threshold temperatures in Ia, Ib, Ic, XXIVa and XXIVb.

Pyrolysand (1.0 g.)	T(CO_2)	T(unsats.)	T(Me.CHO)
Ia	305	305	310
Ib	300	285	310
Ic	300	285	300
XXIVa	310	380	310
XXIVb	300	365	300

Comparison with the corresponding values in the linear polyester II (Table 6) shows T(CO_2) to be slightly higher in the resins. Ib and Ic show a decreased value of T(unsats.), while in Ic it is the same as that in II. T(Me.CHO) values show little variation between I and II.

Threshold temperatures of the resin poly(neopentylene fumarate - methyl α-methylacrylate) are also listed in Table 7. Samples XXIVa and XXIVb were prepared using respectively 0.1 mole % benzoyl peroxide and 0.1 mole % azodicyclohexanecarbonitrile. Comparison of the resin threshold temperatures with those of the corresponding linear polyester XXI (Table 6) shows a slight increase in $T(CO_2)$ and and T(Me.CHO) and a marked increase in T(unsats.).

There is no very obvious reason why the resins I and XXIV should in general show higher threshold temperatures than the parent polyesters II and XXI. In regard to $T(CO_2)$, saturation of fumarate residues would be expected to raise the value only in the unlikely event of all fumarate units participating in cross-linking, thereby precluding primary C^2 in the resin. A^1 is not obviously affected by cross-linking, and the higher resin values of T(unsats.) and T(Me.CHO) are difficult to explain. One factor which may partly account for the increased values is slower diffusion of products out of the cross-linked resins, resulting in a time lag and increase in determined temperature between pyrolytic production and detection of the products. If catalyst residues in the resin have any effect, it would be expected to facilitate rather than retard breakdown and thus lead to lower threshold temperatures in the resins. As far as I and II at least are concerned, the differences are not

great and probably derive from different diffusion rates rather than from any fundamental difference in the mode of breakdown.

XXIVa shows consistently slightly higher values than XXIVb and Ia has a higher T(Me.CHO) value than Ib and Ic. Otherwise, the amount or nature of the catalyst does not significantly affect resin threshold temperatures. This is not unexpected, since these factors should influence only the size of the molecule, which apart from diffusion considerations has no apparent bearing on the threshold temperature. It is not improbable, however, that catalyst residues may play a part in initiating resin breakdown, and this in conjunction with diffusion rate considerations may account for the observed minor differences.

In determination of T(unsats.) for I and XXIV a cold trap prevented entrainment of methyl α-methylacrylate into the detector system. The cold trap was removed to allow determination of monomer liberation temperatures, T(MMA), in the copolymers and III itself. The values are listed in Table 8.

Comparison of the results in Table 8 with the liberation temperatures of products from residual unsaturated polyester units (Table 7) confirms that the initial resin breakdown is monomer liberation from the methylacrylate chain.

Table 8 - Methyl α-methylacrylate liberation temperatures in III, XXIII, Ib and XXIVb.

Pyrolysand (1.0 g.)	T(MMA)
III	240
XXIII	250
Ib	265
XXIVb	260

The T(MMA) value in III is in fair agreement with Grassie's work[7], but there is no apparent explanation of the higher temperatures required in the copolymer XXIII and the resins Ib and XXIVb. Diffusion control may account for the higher temperatures in the resins, but not in the linear XXIII where, however, the increase is less marked, and may not altogether be outwith experimental error.

2.3. Conclusions.

Throughout the text of Section 2.1. attention has been drawn to points of special interest in breakdown of simple ester model compounds; for example, the confirmation of primary C^2 in α-unsaturated esters, competitive B^1 and B^2 in ethyl and methyl acrylate but not in methyl crotonate,

the novel I-A in phenyl acrylate and phenyl α-methylacrylate, and the isomerisations detected in pyrolysis of methyl fumarate and methyl maleate. It now remains to relate the work on simple esters, linear polyesters and resins to the eventual aim of this work - improvement of the thermal stability of a typical unsaturated polyester resin.

The vapour phase pyrolysis of simple model compounds indicated reasonably accurately the observed breakdown of the polyester II. In the resin I this breakdown was found to be preceded by liberation of monomeric methyl α-methyl-acrylate, so that the first consideration in improving thermal stability is the prevention of this depolymerisation reaction. The practical applications of Grassie's technique[7] of reducing the number of initiating unsaturated chain ends by polymerising in a chain transfer solvent are worthy of investigation. Monomer liberation might also be suppressed by a suitable free radical inhibitor, though difficulties would be encountered in dispersing the inhibitor throughout the insoluble resin. Since the evidence indicates α-methylacrylate depolymerisation to terminate at a fumarate unit, it follows that monomer liberation will be decreased by increased cross-linking of the α-methylacrylate chains.

There is no reason why unsaturated polyester segments between cross-links in I should not break down in the same manner as does II itself. The decreased mobility of the

resin may hinder further condensation of polyester end-groups, but cross-linkage between residual fumarate units is likely to occur. Such cross-linkage should improve the thermal stability, since by saturation of the double bonds it precludes primary C^2 of these units. Similarly, saturation of fumarate bonds by copolymerisation in the α-methylacrylate chain precludes primary C^2, as well as being effective in reducing α-methylacrylate depolymerisation.

It is apparent that the overall thermal stability may be improved by increased cross-linking, and that from this view-point the ideal resin would be one which contains a maximum number of cross-links in the α-methylacrylate chain and in which every fumarate unit is copolymerised in an α-methylacrylate chain. There are, however, other practical considerations. Even an incompletely cross-linked resin is too inflexible for convenient handling and saturated units are incorporated to space out the double bonds. There is some evidence that these saturated units are more susceptible to A^1, but this point has not been fully investigated.

C^2 is possibly a free radical reaction and, like depolymerisation, might be suppressed by dispersion of a suitable inhibitor in the resin. There is, however, no apparent method of suppressing A^1 apart from structural modifications to exclude available β-hydrogen atoms. The linear poly(p-phenylene fumarate) has been shown to have good

thermal stability and might form a useful resin if it could be induced to copolymerise. The resin formed by poly(neo-pentylene fumarate) is more thermostable than I, and since supplies of 2:2-dimethylpropan-1:3-diol (which is condensed with maleic anhydride to form the linear polyester) are likely to become more readily available, this resin is of considerable interest. It may unfortunately be impracticable on account of its having a lower softening point than I of comparable constitution; thus, the linear poly(neo-pentylene terephthalate) is more thermostable than poly(ethylene terephthalate) but is useless in synthetic fibre production because of its lower softening point[87].

Future work might well include an investigation of the effect of structural modification upon other properties as well as thermal stability. Thermal degradation in air rather than in an inert atmosphere should also be considered. Quite apart from combustion, there may be catalytic effects, as reported[59] in pyrolysis of poly(ethylene terephthalate) in presence of oxygen traces.

Work more immediately related to that described in the present study is being carried out in these laboratories. The pyrolysis of anhydrides and saturated dibasic acid esters in relation to the breakdown of I is being investigated[66], and new experimental techniques are expected to yield more quantitative[13] and kinetic[88] information on ester pyrolysis.

3. EXPERIMENTAL

3.1. Apparatus and Procedure.

3.1.1. Flow pyrolysis system.

The flow pyrolysis system used extensively in qualitative and semi-quantitative work is shown in Figure 4.

The pyrolysand, normally liquid, is contained in a dropping-funnel which has a nitrogen inlet at the top and a pressure equalising side-arm. The funnel is fitted vertically above the reactor and the pyrolysand feed rate controlled by a stop-cock. Evaporation of volatile liquid pyrolysands is minimised by use of a water-jacketed funnel; polymers and solids melting below ca.150^0 are rendered mobile by an electric heating tape wound round the funnel.

Higher melting solids are introduced to the reactor in small pellet form from a closed horizontal limb containing an iron bar behind the pellets. By moving a magnet outside the limb, the pellets are propelled by the iron bar so that they drop singly into the reactor at fixed time intervals.

Figure 5 shows the three different types of Pyrex glass reactors used. Type 1, for pyrolysis of low molecular weight materials, has a central "contact" space normally packed with 1 in. lengths of 0.25 in. bore Pyrex tubing (contact volume 220 ml.) but on one occasion with copper

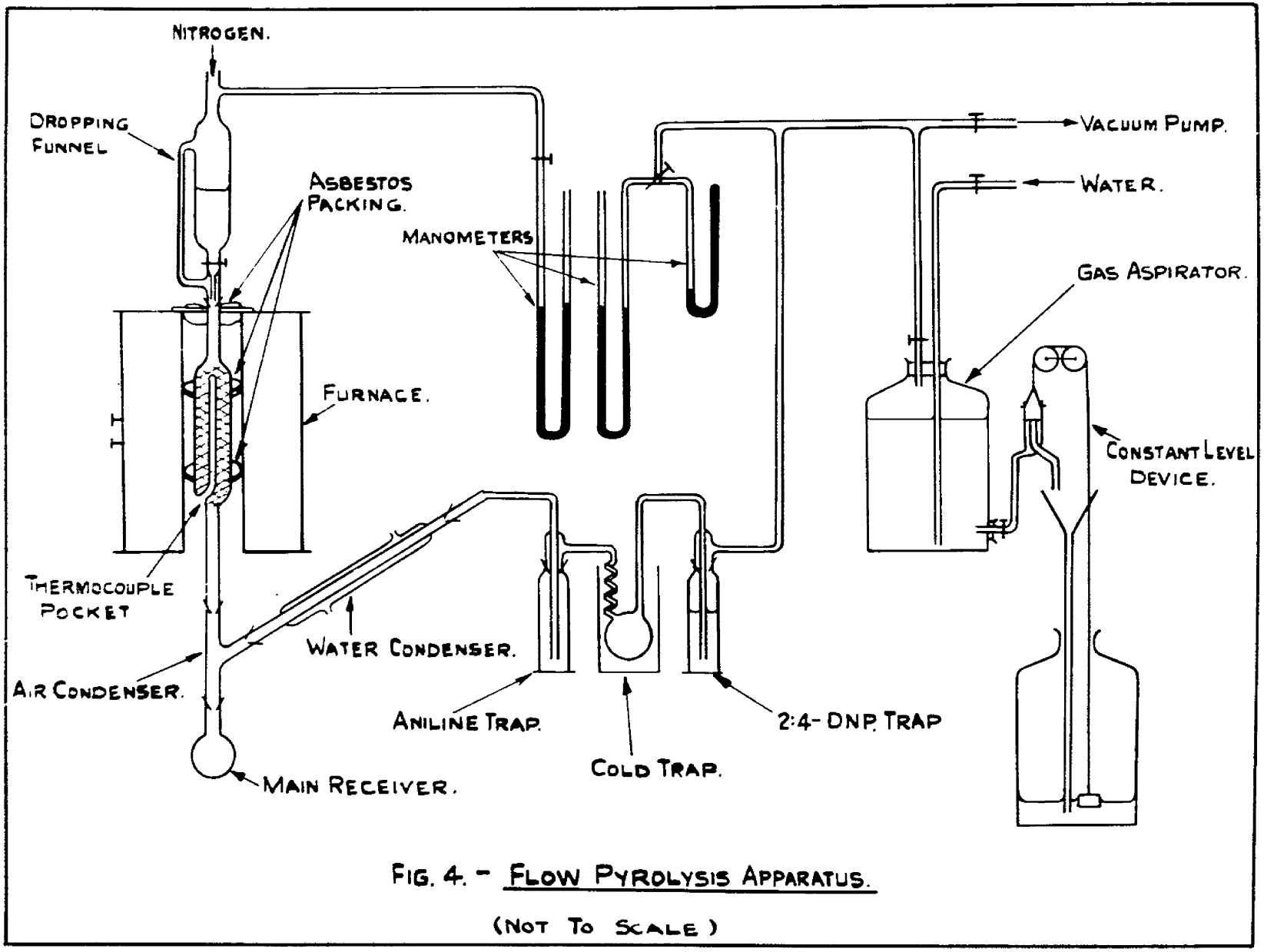


FIG. 4. - FLOW PYROLYSIS APPARATUS.

(NOT TO SCALE)

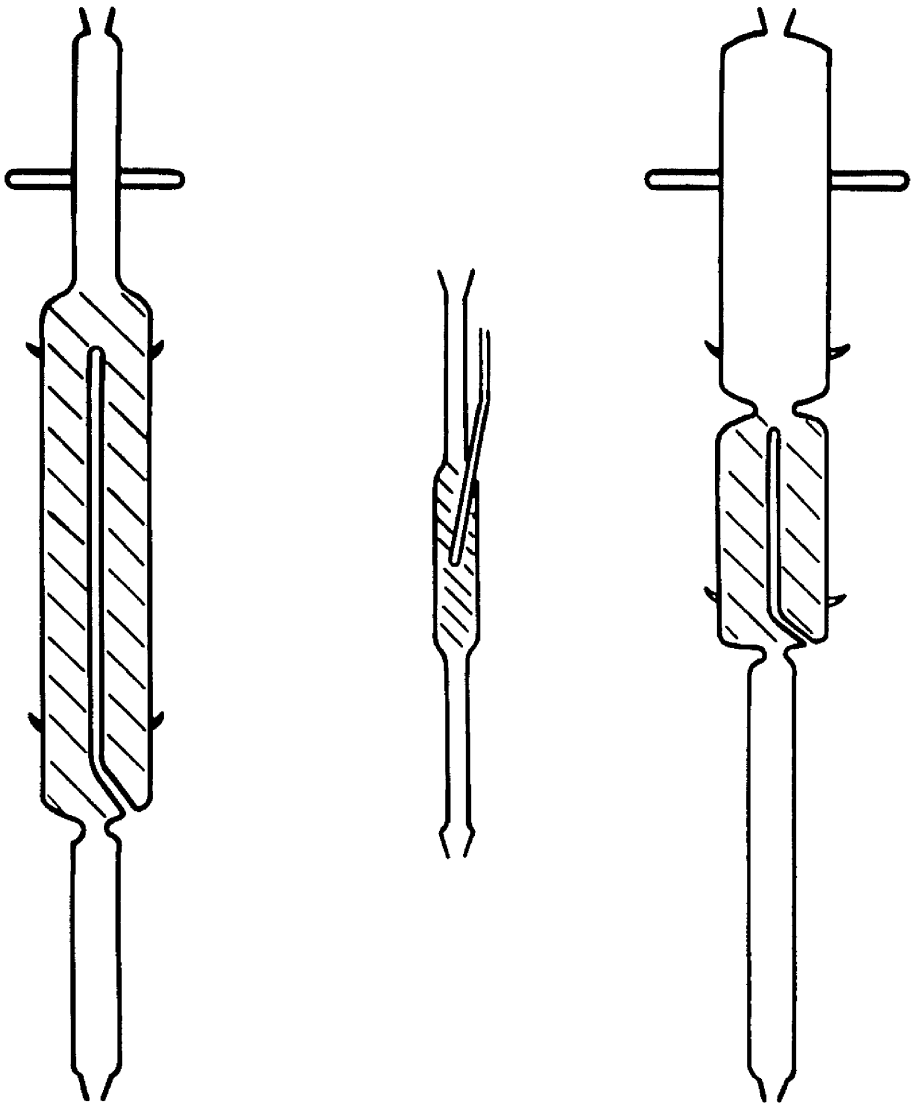


FIG. 5 - FLOW PYROLYSIS REACTORS.

(SHADED AREAS REPRESENT PACKED SECTIONS. SCALE = 1CM. REP. 1 INCH.)

turnings (contact volume 270 ml.). It is supported vertically in an electric furnace L by projecting lugs. Asbestos cord wrapped round small projecting hooks eliminates convection currents by closing the space between reactor and furnace walls, and also serves to hold the reactor in a central position. A thermocouple pocket is fitted such that temperature may be measured at any point on the vertical axis of the reactor packed section.

Reactor type 2 is designed for pyrolysis of polymers, in which frequently extensive cross-linkage and carbonisation tend to block the reactor. It has wider bore above the packed section, which is shorter than in type 1 and is packed with 0.75 in. lengths of 0.5 in. bore Pyrex tubing (contact volume 120 ml.). In other respects it resembles type 1 and is heated in the same furnace L.

A smaller reactor, type 3, is used for small amounts (ca. 10 g. or less) of low molecular weight pyrolysands, or where shorter retention time is desired. Of the same general design as types 1 and 2, it is packed with 0.5 in. lengths of 0.25 in. bore Pyrex tubing (contact volume 20 ml.) and is heated in a smaller electric furnace S.

Except for non-volatile polymer residues, the pyrolysate emerges from the reactor in the vapour phase and is fractionally condensed in a number of receivers. Air-condensed pyrolysate is collected in a receiver vertically

below the reactor; water-condensed products may be collected separately but are generally of small amount and are best returned to the first receiver. Condensation is completed in an acetone-Drikold trap (referred to hereafter as the cold trap). The gaseous pyrolysate is collected over water with an upper layer of liquid paraffin in a 20 l. aspirator fitted with a constant level device to maintain atmospheric pressure.

A trap containing ca. 0.5 ml. aniline is included after the water-condenser to collect ketens as anilide derivatives, their detection being otherwise difficult. Volatile aldehydes entrained beyond the cold trap are removed from the gas stream by a solution of 2:4-dinitrophenyl hydrazine in twice normal hydrochloric acid and ethanol (referred to hereafter as the 2:4-DNP trap).

Furnace L has a winding of 30 ohms resistance round an 18 in. long, 2 in. bore silica tube enclosed in a 10.5 in. diameter asbestos wool-packed aluminium case with Sindanu ends. Temperature is regulated to $\pm 5^{0}$ by a Sunvic energy controller and is measured by a chromel-alumel thermocouple. Experiments on the temperature distribution along the vertical axis of furnace L (empty, top end closed by asbestos packing) showed a wide range, with maximum temperature 4 in. from the top. Measurements during pyrolysis indicated that with the constant vapour flow through the reactor (type 1), temperature distribution on the vertical axis of the packed section

is fairly even. Maximum temperature was recorded at the top of the packed section and pyrolysis temperatures therefore measured at this point. A reading of 500 ± 5° at this point is equivalent to 490 ± 5° at the bottom of the packed section (Figure 6).

Similar considerations led to pyrolysis temperatures in reactor type 2 being measured at the top of the packed section.

Furnace 3 resembles 1 in construction. Temperature in reactor type 3, used in 3, is measured at the mid-point of the packed section, there being little likelihood of a significant variation in temperature throughout such a small volume.

Pressure in the system is measured above the dropping-funnel, so that a blockage in any part of the apparatus may be detected. Gas pressure at the aspirator entry is also measured, and a manometer is fitted to indicate vacuum pressure in removal of oxygen from the apparatus.

Removal of oxygen from the apparatus before pyrolysis is normally achieved by successive evacuations and flushing with nitrogen, introduced *via* alkaline pyrogallol and concentrated sulphuric acid traps. In pyrolysis of volatile materials, the system is evacuated only once and oxygen removal completed by continuous nitrogen flushing for 2-3 hours. The reactor temperature is allowed to settle to a

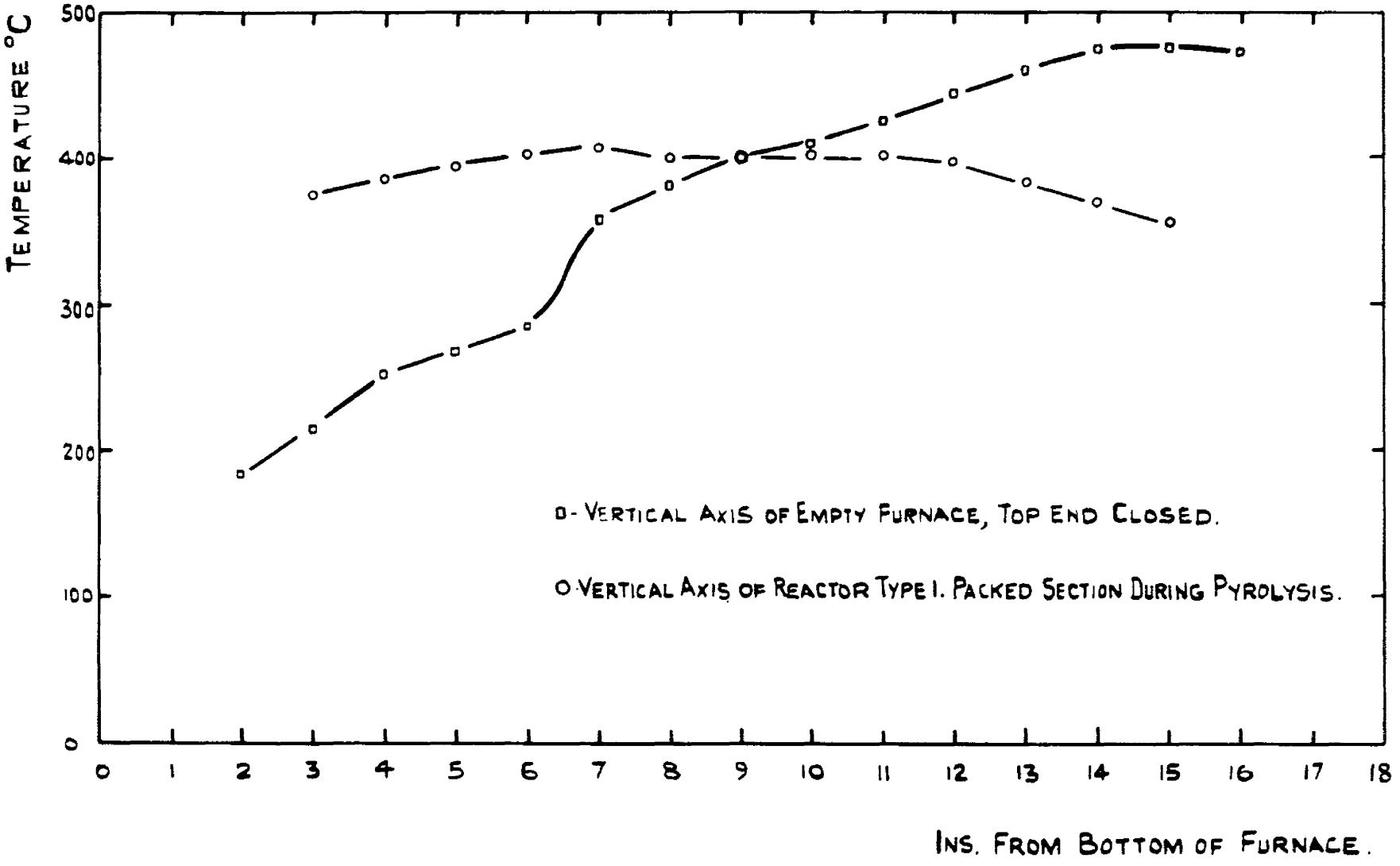


FIG. 6 - TEMPERATURE DISTRIBUTION GRAPHS.

constant value before nitrogen flow is discontinued and the pyrolysand introduced. Feed rate is measured in g./minute so that retention time may be calculated from the equation[69]:

$$\text{Retention time, } t \text{ (seconds)} = \frac{3600 \times 273 \times V_c}{22400 \times (N_R + N_{N_2}) \times T}$$

$$= \frac{43.9 \times V_c}{N_R \times T},$$

where V_c = contact volume, ml.,

N_R = moles pyrolysand/hour,

N_{N_2} = moles nitrogen/hour,

= 0 in this case,

and T = temperature, ^oK.

Carbonaceous or tarry deposits, encountered especially in pyrolysis of polymers, are removed from the reactor before each run by washing with mixed solvents and then heating at 500° in an air current.

3.1.2. Static pyrolysis system.

A number of melt phase pyrolyses of polymers was carried out in a static apparatus, in which reactors type 4 and 5 are used. Type 4 is simply a 5 in. long, 1 in. bore Pyrex tube closed at one end; type 5 is a 50 ml. Pyrex

flask with three necks for nitrogen inlet, thermocouple pocket and take-off condenser. Type 4 is heated in furnace L, with the thermocouple junction strapped with asbestos cord to the lower (closed) end of the vertically supported reactor so that it is at the "hot spot" of the furnace, 4 in. from the top. The asbestos wrapping again eliminates convection currents and holds the reactor central. Type 5 is heated in a bath of Wood's metal, the thermocouple junction being situated below the pyrolysand level.

Pyrolysis products are collected as in the flow system and a similar oxygen-removing procedure adopted.

3.1.3. Threshold temperature determination system.

The apparatus designed for determination of threshold temperatures is shown in Figure 7.

The pyrolysand, ca. 0.01 moles of low molecular weight compounds and ca. 1 g. of polymers, is contained in a reactor type 4, set up in furnace L as already described. Nitrogen is led to the bottom of the reactor, pressure being measured by a manometer.

A reflux condenser connects the reactor to the detector system. In this, a light beam from a 150 watt lamp connected via a mains voltage stabiliser is transmitted through a converging lens and a reagent vessel to a photo-

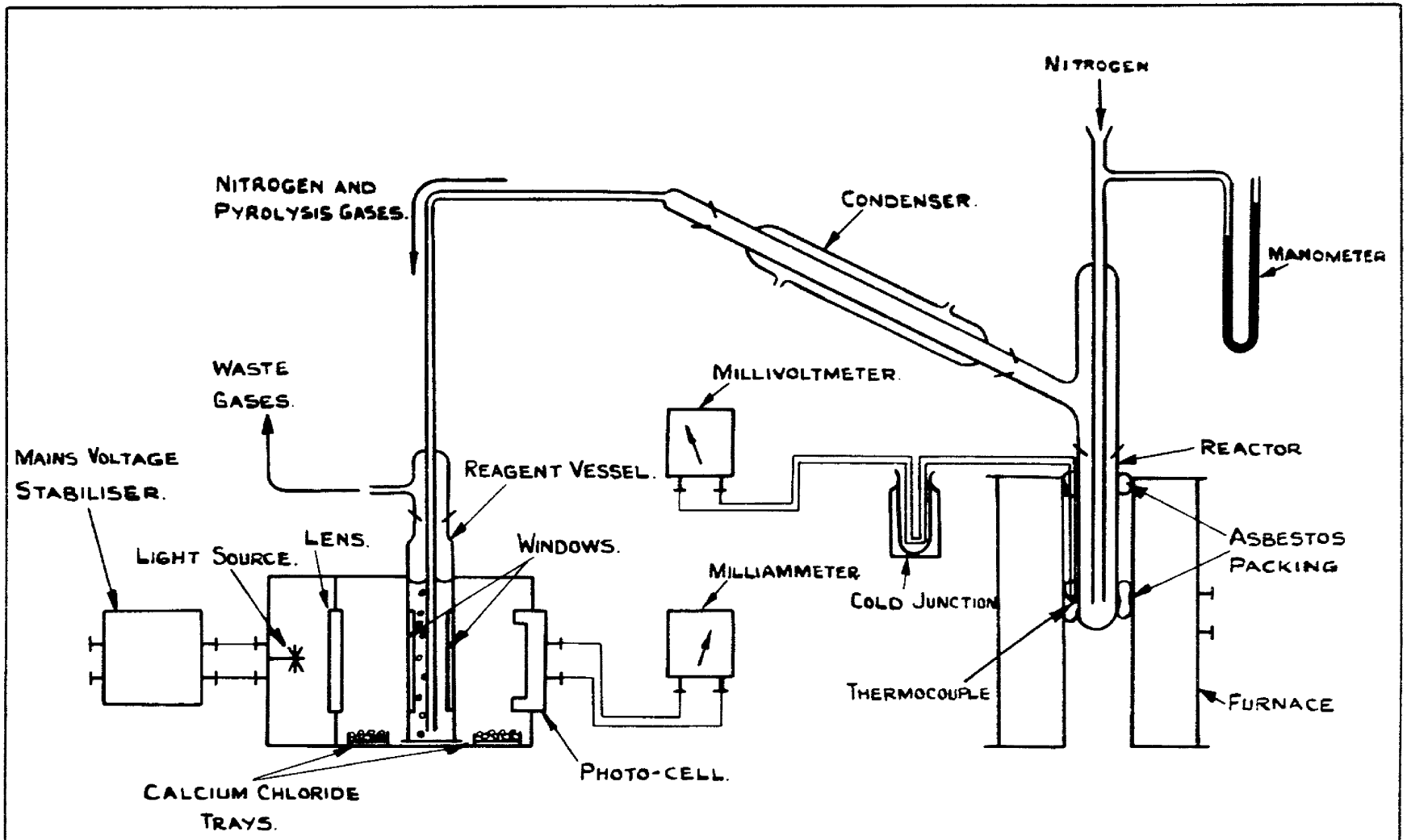


FIG. 7 – THRESHOLD TEMPERATURE DETERMINATION APPARATUS.

(NOT TO SCALE.)

electric cell. The glass reagent vessel, painted black with two opposing windows, contains 185 ml. of a solution which reacts with a particular gaseous pyrolysis product so that its light transmitting properties are altered. This alteration is detected by a micro-ammeter picking up the photo-cell output. Two 500 micro-Farad condensers connected in parallel across the micro-ammeter reduce excessive fluctuation of the value resulting from bubbling of the gases through the reagent vessel. Calcium chloride trays are positioned to eliminate misting of the windows as the light source generates heat, and the whole light-transmitting system is enclosed in a black cover.

Before pyrolysis is commenced, oxygen is removed from the apparatus by the standard procedure (p.87). Nitrogen is then allowed to flow through the system at a rate of 0.1 l./minute, giving a pressure drop of 9-10 mm. Hg across the apparatus, for 30-60 minutes while the micro-ammeter settles to a constant value. With nitrogen flow continuing, the reactor temperature is then raised by 5-6°/minute up to 250° and thereafter by 1-2°/minute. The reflux condenser prevents loss of volatile materials from the reactor but gaseous products liberated at the onset of pyrolysis are swept by the nitrogen stream into the detector system. Reaction between a particular gas and reagent solution alters the micro-ammeter reading and indicates that

the threshold temperature of the reaction producing that gas has been reached.

In practice, micro-amps and temperature values are taken at 5 minute intervals up to 250° and thereafter at 2 minute intervals. A graph of micro-amps vs. temperature is drawn and deviation of the initially constant micro-amps value indicates the threshold temperature.

The apparatus has been successfully used in detection of (1) ethylene and acetylene, (2) carbon dioxide and (3) acetaldehyde. These products are detected respectively by (1) a 0.143% solution of bromine in carbon tetrachloride (resulting in decoloration and increased micro-amps value), (2) a 90% saturated aqueous calcium chloride solution and (3) a 90% saturated solution of 2:4-dinitrophenyl hydrazine in twice normal hydrochloric acid and ethanol (both solutions becoming turbid and reducing the micro-amps value). The liberation of monomeric methyl α-methylacrylate from its polymer and copolymers is also detected by the bromine solution. In detection of both methyl α-methylacrylate and acetaldehyde, an air condensor replaces the normal water-condensor so that return of the product to the reactor is reduced. Since detection of both these products is confined to polymers there is no loss of pyrolysand.

An alkaline solution of potassium iodomercurate[90] was used in an attempt to remove small amounts of acetylene from

gaseous pyrolysates containing also ethylene, thereby allowing detection of ethylene alone. Under the working conditions acetylene removal was incomplete, but since only small amounts are present in the gaseous pyrolysates investigated the recorded threshold temperatures may be considered as pertaining essentially to ethylene. Difficulties were also encountered in finding a suitable reagent for carbon monoxide. Palladium chloride and iodine pentoxide solutions were found to react too slowly; colour changes in blood solution are not detectable in the apparatus. Unless some other reagent is found, it is thought that a modification of this type of continuous apparatus whereby the spectrum changes in carboxylated blood might be detected offers the best method of determining carbon monoxide liberation temperatures.

It is estimated that accuracy limits of $\pm 5^{0}$ are imposed by control and measurement of temperature. Experiments showed less than 1% of the gaseous products to cause an appreciable change in the light transmission of the appropriate solution. Threshold temperatures of different routes can therefore be fairly compared, since differing reaction rates between gas and solution do not significantly affect the results. Preliminary work established the optimum nitrogen flow rate as 0.1 l./minute. At this rate it does not itself, after cooling in the condenser, affect

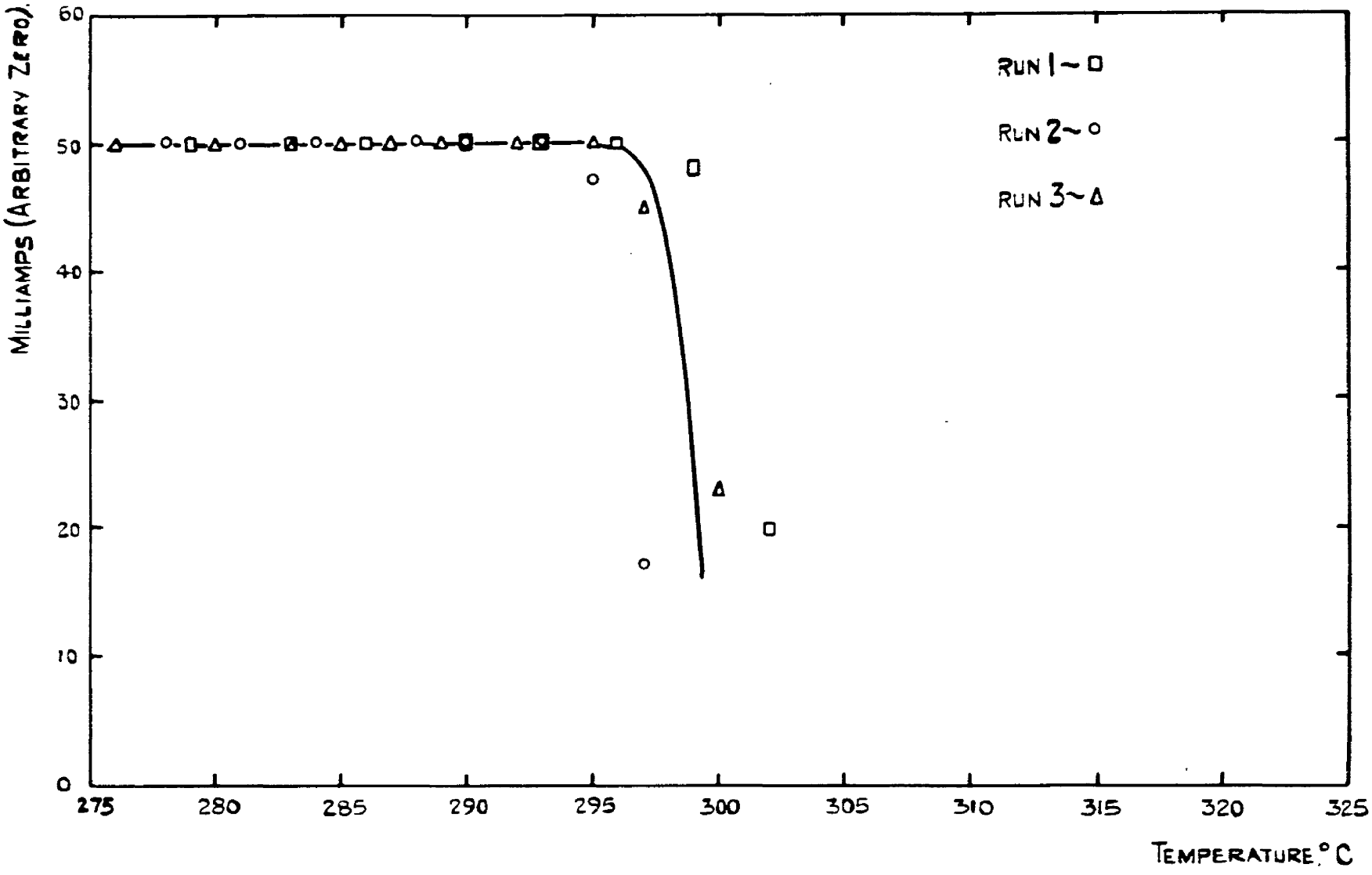


FIG. 8a – CARBON DIOXIDE LIBERATION TEMPERATURE IN POLY (ETHYLENE FUMARATE.)

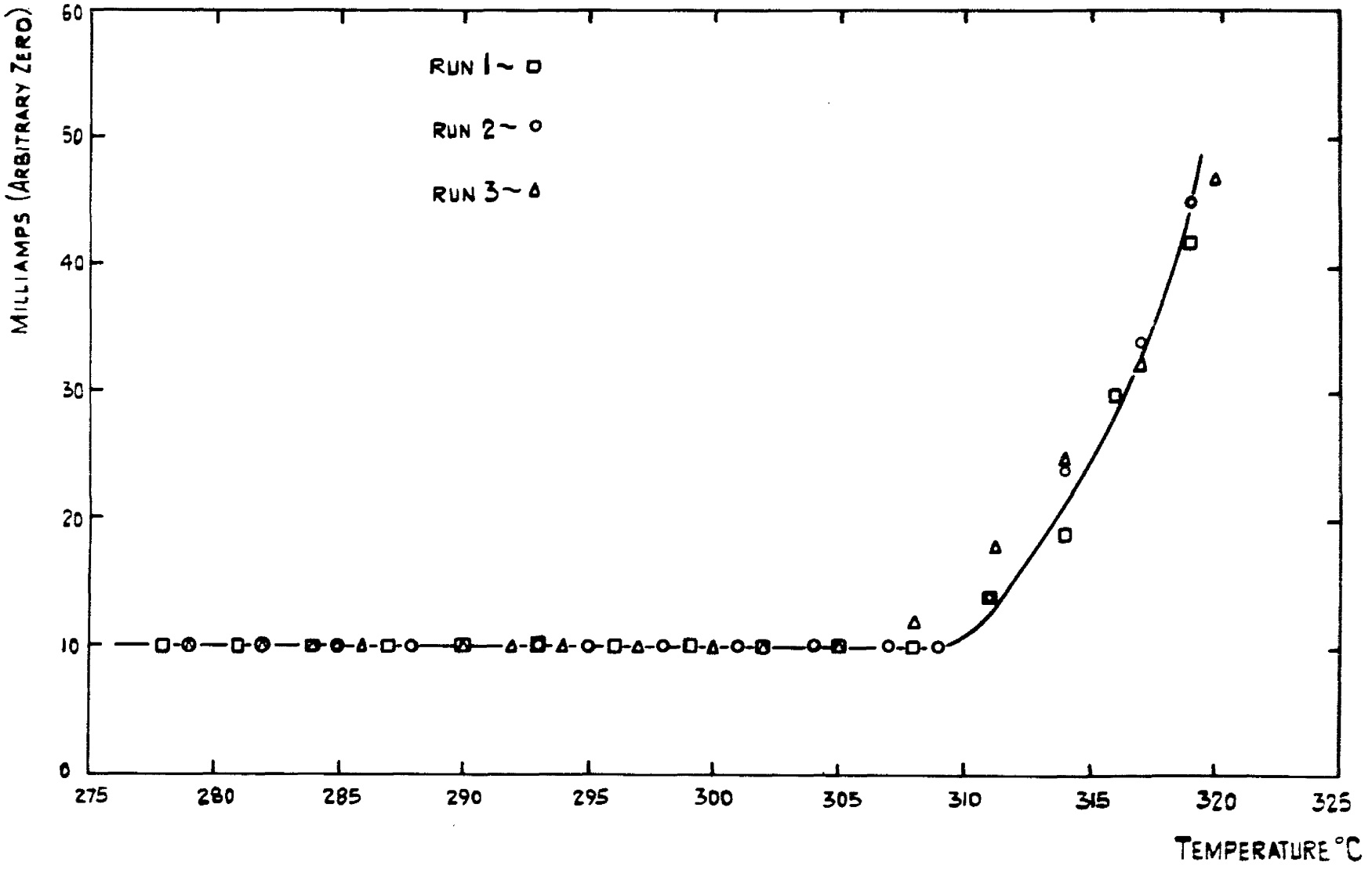


FIG. 8b - ETHYLENE AND ACETYLENE LIBERATION TEMPERATURE IN POLY (ETHYLENE FUMARATE.)

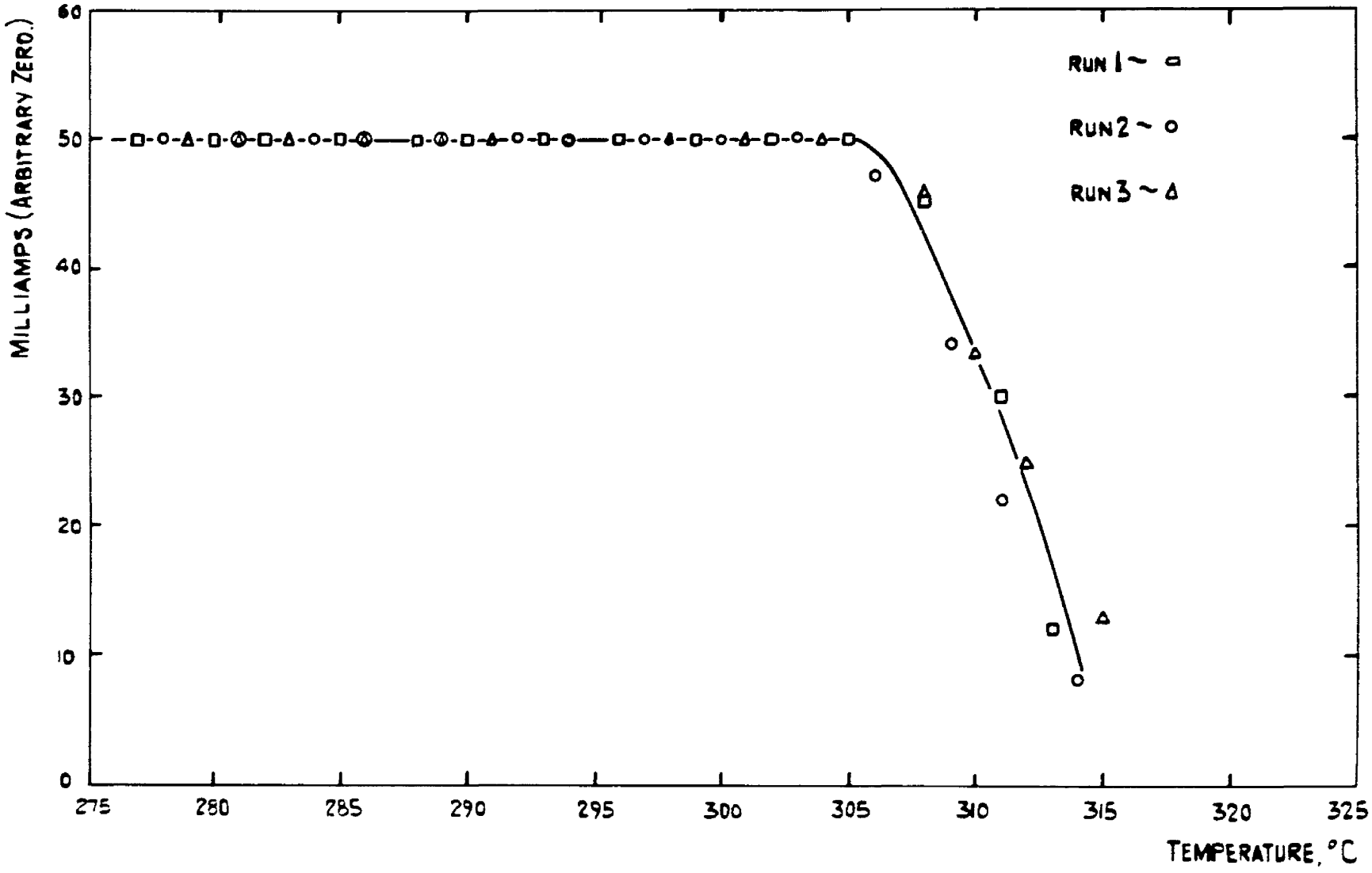


FIG. 8c - ACETALDEHYDE LIBERATION TEMPERATURE IN POLY (ETHYLENE FUMARATE.)

the reagent solutions, and with the system volume reduced to a minimum is fast enough to ensure that the time lag between liberation and detection of products is not sufficient to introduce any error. The condensers across the micro-ammeter reduce fluctuation and allow a more accurate reading without any appreciable loss of sensitivity.

Graphs reproduced in Figure 8 illustrate threshold temperatures of liberation of ethylene and acetylene, carbon dioxide and acetaldehyde in pyrolysis of poly(ethylene fumarate). The change in micro-amps value is clearly sharp and well defined. Each graph is drawn from three runs in which reproducibility within $\pm 5^{\circ}$ is attained.

The apparatus has a wide applicability in that many common pyrolytic reactions yield one or more gaseous products, which may be detected by a suitable reagent. It is proposed that in future use of the apparatus graphs will be automatically drawn by simultaneous recordings of micro-amps and temperature.

3.2. Preparation and Purification of Pyrolysands.

3.2.1. Preparation.

The following pyrolysands were synthesised:

Phenyl acrylate (VIII).

A method described by Tong and Kenyon[91] for the preparation of phenyl α-methylacrylate was adapted for VIII with modifications to reduce losses by polymerisation.

Acrylic acid (containing p-toluquinone inhibitor) and benzoyl chloride in molar ratio 1:2 were mixed and heated to 100° to yield acryloyl chloride, collected in a flask containing a little hydroquinone inhibitor and redistilled (b.72°). Equimolar quantities of acryloyl chloride and phenol were mixed and heated for ca.60 minutes on a water-bath, 10% hydroquinone (by weight of acryloyl chloride) being added as hydrogen chloride evolution diminished. The crude phenyl acrylate product was cooled, dissolved in ether, washed several times with 5% sodium hydroxide solution and then with water. Any polymerisation-catalysing peroxide traces in the ether were removed by washing with acidified ferrous sulphate solution. After a final washing with water and drying over calcium chloride, ether was removed under vacuum and phenyl acrylate distilled at reduced pressure over copper turnings. Yield, ca.65%; b. 87-94°/12 mm., n_D^{20} 1.523. Lit., Filachione et al.[76], b. 87-94°/12 mm., n_D^{20} 1.520.

Phenyl α-methylacrylate (IX).

A similar method starting with inhibited α-methylacrylic acid was used. Yield, ca.60%; b. 98-102°/12 mm.,

n_D^{20} 1.515. Lit., Filachione et al.[76], b. 47-50°/0.2 mm., n_D^{20} 1.5147; Du Pont[92], b. 87-93°/4 mm.

Phenyl formate (X).

In the preparation described by Adickes et al.[31] glacial formic acid (220 g.), phosphoryl chloride (224 g.), phenol (94 g.) and aluminium chloride catalyst (3 g.) were mixed, allowed to stand at room temperature for 90 minutes and then heated for 6 hours at 70-80° on a water-bath to complete the reaction. The product was twice extracted with ice-cold water and the crude phenyl formate residue dissolved in ether. Remaining phenol traces were converted to phenyl benzoate by addition of a little benzoyl chloride and one drop stannic chloride catalyst. After drying over magnesium sulphate, ether was removed under vacuum and phenyl formate twice distilled at reduced pressure, the final product being neutral and negative for phenol (ferric chloride test). Yield, ca. 12 g., 10%; b. 82-83°/15 mm. Lit., Adickes et al.[31], b. 82-83°/15 mm.

Ethylene diacrylate (XIII).

A patented method[93] was modified to reduce losses by polymerisation.

Ethylene glycol (31 g.) and acrylic acid (86 g.) were slowly heated to 180° with inhibitors powdered copper (2 g.)

and hydroquinone (2 g.) and esterification catalyst concentrated sulphuric acid (8 g.). The reaction was conducted under carbon dioxide, eliminated water and a little acrylic acid being removed *via* a water-condenser. On cooling, the reaction mixture was distilled at 3-4 mm. The fraction boiling below 80° was discarded, being mainly water and unchanged reactants; the crude product, boiling above 80°, was washed with water and sodium bicarbonate solution until neutral and then with brine. 2% copper chloride inhibitor was added and the product distilled at reduced pressure.

Esterification under carbon dioxide and, to a lesser extent, in presence of hydroquinone reduced initially encountered losses by polymerisation. Yield, *ca.* 33 g., 25%; b. 65°/1 mm., 90-94°/3 mm., n_D^{20} 1.455. Mt., Burtle *et al.*[94], b. 62-65°/0.9 mm., n_D^{20} 1.455-7; I.O.I., Ltd. and Hill[93], b. 90-94°/2-3 mm., n_D^{20} 1.455.

Vinyl acrylate (XIV).

An ester interchange method originally described by Adelmann[95] was used, 34 g. acrylic acid and 142 g. vinyl acetate being refluxed for 4 hours at 80° with reaction catalysts 0.5 g. mercuric acetate and 0.2 g. concentrated sulphuric acid. A trace copper acetate polymerisation inhibitor was added; it has been shown[88] in a similar preparation of vinyl benzoate that excess copper acetate

lowers the reaction yield. On cooling, excess acid was neutralised with sodium acetate, which was filtered off before distillation of the product. The fraction boiling 90-100° was collected and redistilled to give the pure ester. Yield, 7 g., 15%; b. 94-96°. Lit., Bauer and Kautter[96], b. 94-96°.

Poly(ethylene fumarate) (II).

A method described by Carothers and Arvin[83] and adopted in these laboratories by Grieveson et al.[8,9] was followed.

Maleic anhydride (1.0 moles, twice recrystallised from chloroform) and ethylene glycol (1.05 moles, twice redistilled under carbon dioxide) were mixed in a flask fitted with stirrer, carbon dioxide bubbler and take-off water condenser. After prolonged flushing with carbon dioxide temperature was rapidly raised to and maintained at 195 ± 5°, with continuous stirring and carbon dioxide bubbling. Water of condensation, typically 50% of the theoretical yield within 4 hours, and a little entrained glycol were collected via the condenser.

The resulting polyester is a clear, colourless material which at room temperature may be quite mobile or hard and glassy according to its DP. McMillan[9] has shown that ring formation and cross-linkage are negligible under

these conditions and that the polyester is linear, with DP_n proportional to reaction time at 195 ± 5° as in the graph reproduced in Figure 9. In the present work DP_n was frequently estimated from this graph but on occasion independently determined by cryoscopic measurements or end-group analysis. Table 9 shows good agreement between experimental and graph values of DP_n.

Table 9- Experimental and graph values of poly(ethylene fumarate) DP_n.

Reaction time (hours)	Graph DP_n	Experimental DP_n (end-group analysis)
2	3.9	4.0
3	4.5	4.6
4	5.4	5.2
5	6.4	6.7
6	7.7	7.5

Further work by McMillan indicates that the 0.5 molar excess of glycol adequately compensates for that entrained from the boiling mixture, and that the molar ratio of reactants in the resulting polyester is near unity.

Though early work[97] reports different properties in polyesters prepared from condensation of ethylene glycol

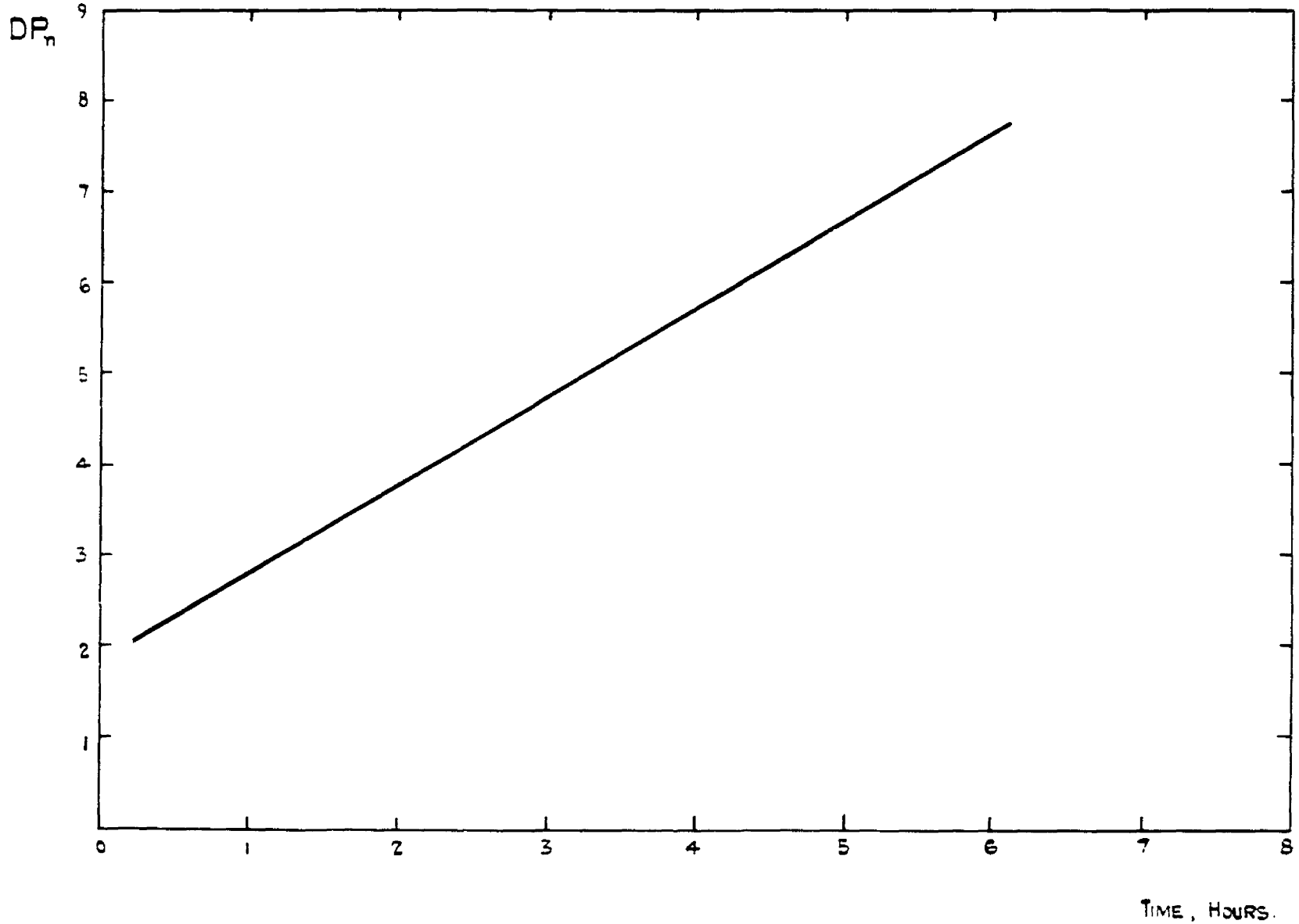


FIG. 9 - PREPARATION OF POLY (ETHYLENE FUMARATE) AT 195 ± 5°

with maleic and fumaric acid respectively, it has recently been shown by Grieveson[8] that the maleic anhydride - ethylene glycol polyester is essentially *trans* in structure. Grieveson found poly(ethylene fumarate) prepared from maleic anhydride and from ethyl fumarate to have similar properties. Batzer and Mohr[79] earlier reported the presence of fumarate linkages in the maleic anhydride product, and polarographic work by Feuer *et al.*[80] concurrent with Grieveson's spectrographic investigations confirms that isomerisation during polycondensation is substantially complete.

During the course of the present study it was confirmed, as previously reported by Vincent[3], that II cross-links on heating in oxygen. In preparation of the polyester, oxygen traces and, to a lesser extent, impurity of reactants resulted in cross-linking after *ca.* 4-6 hours heating. Experiments were also carried out to investigate the possibility of decarboxylation during preparation, this reaction having been reported[42] in polycondensation of saturated dibasic acids with ethylene glycol. By measuring liberated carbon dioxide in a Carbosorb tube, it was found that in preparation of II, DP_n *ca.* 8, carried out under nitrogen, decarboxylation occurred only to the extent of 0.1%. The reaction has therefore a negligible effect on the structure of II.

Purification of II is difficult. The polyester was

dissolved in a large volume of methylene chloride and unreacted anhydride and glycol removed by washing with sodium bicarbonate solution and water respectively. After partial drying over calcium chloride, the solvent was removed under vacuum at 100° with high speed stirring. Negative chlorine tests (Beilstein flame test) showed methylene chloride to be completely removed, but this procedure left traces of water. Throughout this work low DP samples were used to simplify analysis of the pyrolysate, and some further polycondensation during removal of methylene chloride is possible. II is hydroscopic[83], and it is thought that unless a high DP sample is used complete removal of water is impossible.

Low DP_n samples (DP_n ca. 4 or less) are conveniently poured, but samples of higher DP_n are best handled by cooling in acetone-Drikold and chipping into fragments.

Inhibited II samples were prepared by dissolving the appropriate weight of inhibitor in the methylene chloride solution and purifying the polyester as described above, but avoiding washing with sodium bicarbonate solution which would remove phenolic inhibitors. Samples of varying DP_n were withdrawn from the reaction mixture at measured time intervals and DP_n estimated from the graph (Figure 9).

Poly(ethylene fumarate -- methyl α-methylacrylate) (Ia,b,c.).

Commercial methyl α-methylacrylate was purified by

washing several times with 5% sodium hydroxide solution to remove phenolic inhibitors, washing finally with water, drying over calcium chloride and distilling twice under carbon dioxide. A weight of II was dissolved in methyl α-methylacrylate to give a feed ratio[8,9] 0.25 where:

$$\text{Feed ratio, } R = \frac{\text{Moles PEF unsaturation}}{\text{Moles MMA unsaturation}},$$

$$= \frac{\text{Wt. PEF} \times DP_n \times \text{Mol.Wt. MMA}}{\text{Wt. MMA} \times \text{Mol.Wt. PEF}}$$

PEF = Poly(ethylene fumarate); MMA=Methyl α-methylacrylate.

II dissolves readily in methyl α-methylacrylate on heating at ca.60° in a stoppered flask. Copolymerisation was achieved by adding a weighed amount of benzoyl peroxide catalyst, irradiating with ultra-violet light for 1 hour and heating at ca.60° for 1 hour in a closed vessel. The resin was then ground into a fine powder and heated at 100° under vacuum for 4-5 hours, thus ensuring substantially complete removal of unreacted methylacrylate.

Samples Ia, Ib and Ic were prepared using 0.1, 0.2 and 0.5 mole % respectively of benzoyl peroxide.

Poly(neo-pentylene fumarate) (XXI).

2:2-Dimethylpropan-1:3-diol (1.0 moles, recrystallised from ethyl acetate) was condensed with maleic anhydride

(1.0 moles) in the conditions used for preparation of II. Rapid reaction occurred, ca.90% of the theoretical water yield being collected within 3 hours. The resulting polyester is a clear, colourless material which at room temperature is more viscous than II prepared over the same reaction time. For samples of corresponding viscosity at room temperature, XXI softens much more readily than does II, probably because of lower packing density resulting from the lateral methyl groups. Like II, it is soluble in such solvents as benzene, acetone, methylene chloride and chloroform but not in ether.

There is no previous record of the synthesis of XXI. Though it has not been established that it is *trans* in structure, it appears probable that as in preparation of II isomerisation to the fumarate structure may occur. This polyester and XXII (below) are therefore referred to as fumarates.

Poly(*neo*-pentylene fumarate - methyl α-methylacrylate)(XXIVa,b).

XXIV was prepared in the same manner as I, samples XXIVa and XXIVb being catalysed by 0.1 mole % benzoyl peroxide and 0.1 mole % azodicyclohexanecarbonitrile respectively.

Poly(p-phenylene fumarate) (XXII).

Equimolar quantities of hydroquinone (recrystallised from water) and maleic anhydride were reacted under the conditions used in preparation of II. Reaction occurred very slowly but after 4 hours heating a dark-coloured product was obtained. Sublimation of both reactants into the condenser prevented accurate estimation of eliminated water. It was certainly of only small amount, indicating the polyester to be of low DP. This was confirmed by its solubility in 5% aqueous sodium hydroxide solution; acidification reprecipitated the dark polyester so that this is not an apparent solubility resulting from hydrolysis. XXII is only slightly soluble in common organic solvents. It is hard and brittle at room temperatures, softening at ca.100°. Like XXI, XXII has not previously been reported in the literature.

Attempted copolymerisation of XXII with methyl α-methylacrylate failed; this is probably attributable to the presence of unreacted hydroquinone, which could not be completely removed from the polyester by washing or sublimation.

Poly(methyl α-methylacrylate) (III).

III was prepared and purified by the technique adopted for I and XXIV. 0.1 mole % benzoyl peroxide catalyst was

used.

Poly(methyl fumarate - methyl α-methylacrylate) (XXIII).

The same procedure was used to copolymerise 25% (by weight) of methyl fumarate in methyl α-methylacrylate with 0.1 mole % benzoyl peroxide catalyst. XXIII is appreciably less brittle at room temperature than is the pure polymer III.

3.2.2. Purification.

The following commercially available pyrolysands were purified:

Ethyl acrylate (IV), acrylic acid (V), styrene (XI), α-methylstyrene (XII) and methyl acrylate (XVIII).

Phenolic inhibitors were removed by washing several times with 5% sodium hydroxide solution. After finally washing with water and drying over calcium chloride, the pyrolysands were twice redistilled under carbon dioxide and had b.pts.: IV, 101°; V, 140°; XI, 146°; XII, 162°; XVIII, 81°.

Acraldehyde (VI), methyl crotonate (XVI), crotonaldehyde (XVII) and methyl maleate (XIX).

Distillation of the commercial materials yielded

products of b.pts.: VI, 54°; XVI, 122°; XVII, 104°; XIX, 205°.

Methyl fumarate (XV) and fumaric acid (XX).

Recrystallisation from ethanol yielded products of m.pts.: XV, 102°; XX, 287° (subliming, sealed tube).

Ethanol (VII).

Tests for water (Fisher reagent) on spectroscopically pure ethanol were negative and the material was pyrolysed as obtained.

The author thanks Imperial Chemical Industries Limited for gifts of 2:2-dimethylpropan-1:3-diol, ethyl acrylate, α-methylacrylic acid and methyl α-methylacrylate.

3.3. Analysis and Pyrolysis Conditions.

3.3.1. Analytical methods.

Gaseous pyrolysates were analysed by a standard Hempel apparatus, supplemented in most cases by use of an alkaline potassium iodomercurate pipette for specific absorption of acetylene[90]. Alkyne traces were qualitatively detected by precipitation of the red copper derivative from ammoniacal cuprous chloride solution.

Cold trap pyrolysates were allowed to vaporise at room temperature into an aspirator and examined in the gas phase.

Careful fractionation of the liquid pyrolysates at atmospheric or reduced pressure afforded a reasonable separation of products, though volatile aldehydes tended to contaminate higher boiling fractions. Formally possible products could frequently be eliminated on the evidence of boiling ranges. A carbonaceous residue, sometimes containing polymeric materials, normally remained after distillation. Copper acetate and hydroquinone inhibitors were added before distillation to liquid pyrolysates containing products liable to polymerise. Fractionation of polyester pyrolysates was on occasion supplemented by extraction of part of the pyrolysate for detection of minor products.

Solids insoluble in the liquid pyrolysate were filtered off before distillation. Soluble solid products either sublimed during fractionation or remained in the residue. Where phenol was obtained, it did not normally crystallise from the pyrolysate but distilled during fractionation and is hence considered as a liquid product. Separation of solids and liquids in polyester pyrolysates proved impracticable and they were estimated together.

Aniline and 2:4-DNP trap products, if in sufficient quantity, were recrystallised and identified.

Standard chemical methods of identification were employed, all solid products and derivatives being characterised by mixed m.pts. Accurate quantitative analysis was possible only in the gaseous pyrolysates, gravimetric estimation of liquid and solid products being rendered at best approximate by the frequent complexity of the pyrolysates. In certain cases quantitative analysis was made even more difficult by the occurrence of one product in two or more receivers. For example, propene was found mainly in the gas aspirator but condensed partly in the cold trap; formaldehyde formed the solid trimer, trioxane, and like acetaldehyde was also found in the liquid pyrolysate, cold trap and 2:4-DNP trap.

In view of the difficulties of quantitative analysis, only an approximate estimation of the weight contribution of competitive routes to the overall pyrolysand breakdown can be made. The almost invariable occurrence of secondary breakdown complicates this estimation still further, though allowance was made for it by separately investigating breakdown of primary products. This also served to confirm qualitatively the attribution of certain products to secondary breakdown. In a number of pyrolyses where the same end-products are formed *via* alternative routes, the extent of these routes could only be estimated as major, minor or trace.

Standard identification methods were supplemented by

the following special techniques:

Infra-red spectrometry.

A great deal of useful information was afforded by spectroscopic examination of the pyrolysis products. Comparison of the product spectrum with a number of standards yielded rapid and accurate identification. Only in a few cases was the structure of a product deduced from its spectrum without reference to standards.

Infra-red spectrometry facilitated identification of trace components in the gaseous pyrolysates, particularly methane which may otherwise remain undetected if in small amount. Identification of acetylene, methylacetylene, ethylene and propene, especially where two or more of these products occurred together, was conveniently confirmed by this technique. Propene and isomeric butenes, frequently collected with volatile aldehydes in the cold trap, were best characterised by infra-red spectrometry in the vapour phase.

Chemical evidence in analysis of liquid pyrolysates was also supplemented by this technique. Where only trace quantities were obtained, identification of products was based almost entirely on spectroscopic evidence.

The instrument used in this work has been described by Brownlie[93]. Gases were examined in a 10 cm. cell and volatile liquids in a 0.00973 cm. cell. Liquids boiling

above <u>ca.</u>60° were investigated in the form of capillary films between plates and solids in a Nujol mull film. Polymers were also studied as capillary films, or in solution, carbon tetrachloride being the most commonly used solvent. Figure 3 shows examples of polyester film spectra.

All samples were dried over calcium chloride before analysis to avoid damaging the sodium chloride plates and cell windows.

<u>Paper chromatography.</u>

Paper chromatography was applied to the identification of aldehyde and ketone 2:4-dinitrophenyl hydrazones (referred to hereafter as 2:4-DNP's). This technique was particularly useful when pyrolysis yielded more than one carbonyl compound.

Using the method described by Burton[99], Whatman No.1 paper was impregnated with an ethyl tartrate-water-methanol mixture in ratio 1:3:12 (by weight). The paper was then dried; differences in drying time affected the results and derivatives for identification were therefore compared with a number of standards in the same run. A solution of 2% carbon tetrachloride in a 60-80° petroleum fraction was used for elution, giving a reasonable separation despite occasional streaking. The distances travelled by the spots in upward development were compared under ultra-violet light .

Colour tests.

The standard ferric chloride colour test was used for phenols. Esters were detected following hydrolysis with 20% methanolic potassium hydroxide, acidification and addition of hydroxylamine hydrochloride in ethanol, by the violet colour formed on adding ferric chloride solution.

A colour test described by Davidson and Newman[100] was used in detection of linear anhydrides. A temporary green or blue colour is rapidly produced with o-4-benzamidophenyl-acetic acid. The test is conducted in pyridine solution and is not applicable to cyclic anhydrides.

Phenyl formate was indicated by a green colour formed on adding potassium permanganate solution. Naphthalene and 2:3-dimethylnaphthalene formed green colours on addition of aluminium chloride in chloroform and of concentrated sulphuric acid respectively.

Poly(ethylene fumarate) molecular weight determination.

The molecular weight of II was determined cryoscopically in benzene but more commonly by end-group analysis as described by McMillan[9]. A solution of ca. 0.2 g. II in 10 ml. chloroform was titrated against deci-normal alcoholic potassium hydroxide in an ice-bath. Phenolphthalein indicator was used and the end-point taken to be when one

drop of alkali produced a red colour lasting for at least 5 seconds. The average of three runs was taken, reproducibility of molecular weight being within ± 2%.

3.3.2. Flow pyrolysis conditions and yields.

Flow pyrolysis conditions and yields are shown in Table 10 (p.117). Carbonaceous deposits were not weighed unless exceptionally heavy or where comparison with another pyrolysand was desired, but estimated as moderate, small or trace. Cold trap pyrolysates less than ca. 0.5 g. were not easily weighed and are also estimated as small or trace. Phenyl formate (X) and poly(ethylene fumarate) (II) yielded respectively phenolic and polymeric pyrolysates for which a combined liquid and solid weight is given. Where II was pyrolysed in an unpacked reactor, contact volume could not satisfactorily be estimated and no figure for retention time is given. With the exception of fumaric acid (XX), which entered the reactor in small pellet form, all pyrolysands were introduced as liquids.

3.3.3. Flow pyrolysis analytical results.

Gaseous pyrolysates.

In Table II (p.121) gaseous pyrolysates are reported on a nitrogen-free basis.

Cold trap pyrolysates.

Table 12 (p.123) shows room temperature vapour phase analysis of cold trap pyrolysates. The proportion of each product in the pyrolysate is estimated.

Liquid pyrolysates.

Fractions obtained on distillation of the liquid pyrolysates are listed in Table 13 (p.125), pressure being 760 mm. Hg except where otherwise indicated. Figures indicate the boiling range and (in parenthesis) the approximate weight of the fraction in g. The addition of an inhibitor before distillation is shown.

Table 14 (p.128) summarises the analysis of liquid pyrolysate fractions. The amount of each product identified was estimated approximately from the weight of the fraction containing it. The analysis of pyrolysates from inhibited VIII is omitted; it is similar to that of VIII itself, except that in presence of inhibitor (1) phenol and phenyl formate were not detected.

Since methyl fumarate (XV) and methyl maleate (XIX) yielded the same products, they are considered together in Table 14. The only product not common to both is some unchanged cis ester in the pyrolysate from XIX. The polymeric pyrolysate from poly(ethylene fumarate) (II) is included in Table 14 with liquid pyrolysates.

In Table 15 (p.136) the products obtained by extraction of the pyrolysates from IX are shown.

Solid pyrolysates.

Products identified in analysis of solid pyrolysates are shown in Table 16 (p.136). XV and XIX yielded solid products common to both. Small amounts of polymers in otherwise liquid pyrolysates are considered in Table 16 as solids.

Aniline trap products.

Ethylene diacrylate (XIII) yielded a trace aniline trap derivative (Table 10, runs 23-25). Recrystallised from water it had m.pt. 194-197°, but could not be characterised.

2:4-DNP trap products.

Table 17 (p.137) lists the derivatives obtained in the 2:4-DNP trap. XV and XIX are again considered together.

3.3.4. Static pyrolysis conditions and analytical results.

In Table 18 (p.137) experimental data concerning the DP_n increase in II is given.

Table 19 (p.137) shows pyrolysis conditions and

experimental results in comparison of gas evolution from II, XXI and XXII. Reactor temperature was controlled as follows:

(1) Reactor flushed with nitrogen while temperature raised to 150°.

(2) Temperature raised to 250° at a rate of 6°/minute, nitrogen flow continuing.

(3) Nitrogen discontinued, aspirator connected to reactor and reactor temperature raised to 350° at 3°/minute.

(4) Temperature maintained at 350° for 15 minutes.

(5) Gases diverted to exit.

Gases were collected in a 1 l. aspirator fitted with a constant level device.

Pyrolysis conditions and experimental results in comparison of methyl α-methylacrylate liberation from Ia, III, XXIII and XXIVa are shown in Table 20 (p.138). The weight of each pyrolysand was such that, calculated from its known or approximately known composition, it contained 1 g. of methyl α-methylacrylate. Methyl fumarate traces liberated from XXIII are believed to have been present originally as monomer; they sublimed from the polymer as heating was commenced. Water liberated from Ia and XXIVa is also thought to have been present originally in the pyrolysand.

3.4. Miscellaneous.

3.4.1. Synthesis of 2-hydroxyethyl acrylate.

2-Hydroxyethyl acrylate, a formally possible breakdown product of ethylene diacrylate (XLII), was synthesised by reaction of equimolar quantities of sodium acrylate and ethylene chlorhydrin in presence of a little diethylamine catalyst. After refluxing for 3 hours, the product was distilled under vacuum. Yield, 7%; b. 76-78°/2 mm., n_D^{20} 1.446. Lit., Rice and Herzfield[101], b. 75-77°/2 mm., n_D^{20} 1.446.

3.4.2. Reaction of vinyl acrylate with acrylic acid.

Vinyl acrylate (3 g.) was refluxed with acrylic acid (2 g.) for 2 hours at 90-100°. The product contained acetaldehyde (2:4-DNP, m. 159-160°, mixed m. 162-163°) and acrylic anhydride (colour test[100]; infra-red spectrometry, comparison with standard).

3.4.3. Attempted synthesis of but-3-enyl acrylate.

But-1-ene-4-ol was prepared as described by Linstead and Rydon[102] from magnesium turnings and trioxane refluxed in ether with allyl bromide and a little iodine. Refluxing of the alcohol with an equimolar quantity of acrylic acid and a little concentrated sulphuric acid yielded no ester product.

Despite the addition of p-methoxyphenol, hydroquinone and copper acetate inhibitors and refluxing under carbon dioxide, extensive polymerisation occurred.

3.4.4. Dermatitic properties of unsaturated esters.

Previous workers in these laboratories, notably Foxman[65] and Hughes[103], have reported the dermatitic properties of fumarates and maleates. In the present work, the author encountered no difficulty in handling these materials but incurred immediate and severe dermatitis from ethylene diacrylate (XIII). The irritation was confined to the fingers and was not effectively countered by the use of barrier creams or rubber gloves. It was necessary to curtail work on ethylene diacrylate, since the rash abated only on avoiding contact with the ester for one or two weeks, and applying an anti-histamine preparation.

2-Hydroxyethyl acrylate was also found to be dermatitic, but neither it nor ethylene diacrylate sensitised the author to other reputedly dermatitic compounds. The effect of such materials upon different workers appears to be quite unpredictable.

Abbreviations and symbols in Table 10

- = Nil ; T = Trace ; N = Negligible ;
S = Small ; M = Moderate ; † = Prep omitted ;
n = Not investigated ; G = Copper packing ; U = Unpacked ;
P = Precipitate ; V(i)→V(v) = V with inhibitors (i) - (v)

Table 10 - Flow pyrolysis conditions and yields.

Run no.	1	2	3	4	5	6	7	8	9	10	11
Pyrolysand	IV	IV	IV	IV	IV	V	VI	VI	VII	VIII	VIII
Temperature, °C	500	500	500	500	500	500	500	500	500	550	550
Reactor type	3	1	1	1	1	1	1	3	3	1	1
Pyrolysand wt., g.	6	58	69	35	44	12	8	7	13	69	60
Feed rate, g./min.	.31	.30	.40	.33	.34	.46	.25	.23	.31	.33	.38
Retention time, secs.	6	69	52	63	61	32	48	5	3	85	76
Gaseous pyrolysate vol., l. at N.T.P.	1.0	14.8	22.6	8.8	12.7	1.2	2.3	0.4	2.0	3.2	2.2
Cold trap pyrolysate wt., g.	†	2	4	2	2	8	-	-	2	-	-
Liquid pyrolysate wt., g.	7	28	55	25	29	9	5	6	9	66	55
Solid pyrolysate wt., g.	-	-	-	-	-	-	-	-	-	T	T
Aniline trap	-	-	-	-	-	-	-	-	-	-	-
2:4 DNP trap	P	-	-	-	-	-	-	-	-	-	-
Carbonisation, g.	N	N	N	N	N	N	S	S	-	15	14
Pyrolysand destroyed, %	50	96	94	94	98	25	50	40	31	52	51

(contd.)

Abbreviations and symbols in Table 10.

- = Nil	T = Trace	N = Negligible
S = Small	M = Moderate	t = Trap omitted
x = Not investigated	C = Copper pucking	U = Unpacked
P = Precipitate	V(i)-V(v) = V with inhibitors (i)-(v).	

Table 10 (Contd)- Flow pyrolysis conditions and yields.

Run no.	12	13	14	15	16	17	18	19	20	21
Pyrolysand	II	II	X	XI	XII	V (i)	V (ii)	V (iii)	V (iv)	V (v)
Temperature, °C	550	550	550	550	550	550	550	550	550	550
Reactor type	1	1	1	1	1	1	1	1	1	1(c)
Pyrolysand wt., g.	43	48	52	77	46	44	27	15	31	32
Feed rate, g./min.	.28	.30	.36	.36	.26	.35	.34	.30	.30	.32
Retention time, secs.	113	105	61	57	59	83	85	97	97	111
Gaseous pyrolysate vol., l. at N.T.P.	3.2	3.5	10.4	N	N	0.9	1.6	1.4	3.5	5.5
Cold trap pyrolysate wt., g.	-	-	-	-	-	-	-	-	-	-
Liquid pyrolysate wt., g.	38	42	39	76	45	41	25	14	23	22
Solid pyrolysate wt., g.	T	T		T	T	-	T	T	T	T
Aniline trap	-	-	-	-	-	-	-	-	-	-
2:4-DNP trap	-	-	-	-	-	-	-	-	-	-
Carbonisation, g.	5	5	-	-	-	1	2	1	7	11
Pyrolysand destroyed, %	51	46	ca. 100	?	?	9	26	37	67	78

(contd.)

Abbreviations and symbols in Table 10.

0 = Nil ;	T = Trace ;	N = Negligible ;
S = Small ;	M = Moderate ;	† = Trap omitted ;
x = Not investigated ;	C = Copper packing ;	U = Unpacked ;
P = Precipitate ;	V(i)-V(v) = V with inhibitors (i)-(v) .	

Table 10 (Contd.)- Flow pyrolysis conditions and yields

Run no.	22	23	24	25	26	27	28	29	30
Pyrolysand	XIII	XIII	XIII	XIII	XIV	XV	XVI	XVII	XVII
Temperature, °C	400	450	500	500	500	500	500	500	500
Reactor type	3	1	1	1	3	1	1	3	3
Pyrolysand wt., g.	25	30	25	30	7	20	26	5	6
Feed rate, g./min.	.86	.31	.21	.31	.23	.13	.40	.33	.26
Retention time, secs.	14	122	180	122	8	230	52	5	6
Gaseous pyrolysate vol., l. at N.T.P.	8	4.6	6.2	4.8	0.3	2.0	1.7	0.3	0.4
Cold trap pyrolysate wt., g.	-	8	8	8	8	0.5	0.5	?	?
Liquid pyrolysate wt., g.	24	19	11	7	5	3	22	3	4
Solid pyrolysate wt., g.	-	-	3	?	-	11	-	-	-
Aniline trap	-	P	P	P	-	-	-	-	-
2:4-DNP trap	-	P	P	P	P	P	-	-	-
Carbonisation, g.	8	6	7	8	8	3	8	-	-
Pyrolysand destroyed, %	8	63	84	65	57	40	23	40	33

(contd.)

Abbreviations and symbols in Table 10.

- = Nil	T = Trace	N = Negligible
S = Small	M = Moderate	† = Trap omitted
n = Not investigated	C = Copper packing	U = Unpacked
P = Precipitate	V(i)-V(v) = V with inhibitors (i)-(v).	

Table 19 (Contd.) - Flow pyrolysis conditions and yields

Run no.	31	32	33	34	35	36	37	37	39	40	41
Pyrolysand	XVIII	XVIII	XVIII	XIX	XIX	II	II	II	II	II	II
Temperature, °C	500	500	500	500	500	350	400	400	400	400	400
Reactor type	3	3	1	1	1	2(T)	2	2	2	2	1
Pyrolysand wt., g.	10	10	45	20	55	63	36	52	56	64	15
Feed rate, g./min.	.17	.27	.33	.13	.36	2.5	.6	.9	.9	.3	.43
Retention time, secs.	10	6	55	230	91	∞	175	130	108	230	63
Gaseous pyrolysate vol., l. @ N.T.P.	0.4	0.3	7.7	5.3	16.4	0.8	7.0	10.0	9.5	14.0	0.2
Cold trap pyrolysate wt., g.	2	2	1	0.5	2.5	3	2	2	2.5	3	2
Liquid pyrolysate wt., g.	9	9	25	4	16	} 69	} 18	} 26	} 17	} 26	2
Solid pyrolysate wt., g.	-	-	3	9	9						14
Aniline trap	-	-	-	-	-	-	-	-	-	-	-
2:4-DNP trap	-	-	-	P	P	P	P	P	P	P	-
Carbonisation, g.	8	8	8	5	12	8	10	15	26	22	8
Pyrolysand destroyed, %	8	8	49	95	93	8	Ca. 100	Ca. 100	Ca. 100	Ca. 100	8

Abbreviations and symbols in Table 11.

- = Nil ; T = Negligible ; T = Trace ; x = Not investigated ;

† = Identification confirmed by infra-red spectrometry, comparison with standards ;

≠ = R = Me for VI (runs 12,13), otherwise R=H .

Run no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Pyrolysand	IV	IV	IV	IV	IV	V	VI	VI	VII	VIII	VIII	IX	IX	X
CO_2	3	15	15	9	*	23	-	?	?	23	23	38	41	?
CH OR /	65	3	3	2	*	63	45	35	6	15	18	7	9	-
CH_2:CH_2		74	73	78	*					?	?	?	?	-
CO	12	8	9	11	*	12	55	65	15	62	59	55	50	99.5
CH_4	-	?†	?†	?†	*	-	?†	?†	33	-	-	-	-	-
H_2	-	-	-	-	*	-	-	-	66	-	-	-	-	-

Run no.	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Pyrolysand	XI	XII	V (i)	V (ii)	V (iii)	V (iv)	V (v)	XIII	XIII	XIII	XIII	XIV	XV	XVI
CO_2	N	N	99.5	25	21	33	28	-	34	32	35	39	57	43
CH OR /	N	N	?†	23	16	16	29	?†	4	2	1	22	?†	-
CH_2:CH_2	N	N	?†	?†	?†	?†	?†	?†	22	19	16		?†	-
CH_2:CHMe	N	N	-	-	-	-	-	?†	?†	?†	?†	-	10	29†
CO	N	N	?	52	61	51	42	?	40	46	44	39	31	57
CH_4	N	N	-	-	-	-	-	-	?†	?†	?†	?†	?†	-
H_2	N	N	-	-	-	-	-	-	-	-	-	-	?	-

(contd.)

Abbreviations and symbols in Table 11.

\- - Nil ; N - Negligible ; T - Trace ; = - Not investigated ;

† - Identification confirmed by infra-red spectrometry, comparison with standards ;

≠ - R = Me for VI (runs 12,13), otherwise R = H .

Table 11 (Contd.)- Percentage composition of gaseous flow envelopes

Run no.	29	30	31	32	33	34	35	36	37	38	39	40	41
Pyrolysand	XVII	XVII	XVIII	XVIII	XVII	XIX	XIX	II	II	II	II	II	IX
CO_2	1	2	6	20	22	45	57	93	74	80	79	77	69
CH OR ‡	-	-	1	1	1	2	1	7	2	1	1	1	-
CH_2:CH_2	-	-	1	3	1	1	2		5	5	5	6	17
CH_2:CHMe	36	48	51	40	33	14	11	-	-	-	-	-	-
CO	64	52	41	40	45	41	32	-	18	14	15	16	3
CH_4	-	-	1	1	1	1	1	-	1	1	1	1	-
H_2	-	-	1	1	1	1	1	-	-	-	-	-	-

Abbreviations in Table 12

Pyr. - Pyrolysate;

I.R. - Identification by infra-red spectrometry, comparison with standards;

P.C. - Identification by paper chromatography of 2:4-DNP's.

Table 12- Analysis of cold trap pyrolysates.

Run no.	Pyr.	Product	Identification		Amount
4-5	IV	But-1-ene	I.R.		Trace
		Acetaldehyde	2:4-DNP:	m.158-60°, mixed m.160-62°; P.O.	Major
6	V	Acetaldehyde	2:4-DNP:	m.163-64°, mixed m.165°	Total
9	VII	Acetaldehyde	2:4-DNP:	m.165°, mixed m.166°	Total
23-25	XIII	Propene	I.R.		Small
		Buta-1:3-diene	I.R.		Small
		Acetaldehyde	2:4-DNP:	m.164°, mixed m.165°	Major
26	XIV	Buta-1:3-diene	I.R.		Major
		Acetaldehyde	2:4-DNP:	m.160°, mixed m.161°	Small
27	XV	Propene	I.R.		Trace
34-35	XIX	Formaldehyde	2:4-DNP:	m.163°, mixed m.164°	Major
		trans-But-2-ene	I.R.		Small

(contd.)

Abbreviations in Table 12.

Pyr. - Pyrolysand.

I.R. - Identification by infra-red spectrometry, comparison with standards;

P.C. - Identification by paper chromatography of 2:4-DNP's.

Table 12(Cont'd.) - Analysis of cold trap flow pyrolysates

Run no.	Pyr.	Product	Identification	Amount
28	XVI	Propene	I.R.	Trace
		Formaldehyde	2:4-DNP: m.166°, mixed m.166°	Major
		trans-But-2-one	I.R.	Major
29,30	XVII	Propene	I.R.	Total
31-33	XVIII	Propene	I.R.	Trace
		Formaldehyde	2:4-DNP: m.158-59°, mixed m.161-62°; P.C.	Major
36-40	II	Acetaldehyde	2:4-DNP: m.168°, mixed m.168°	Total
41	II	Acetaldehyde	2:4-DNP: m.161°, mixed m.163°; P.C.	Total

Abbreviations in Table 13.

CA = Copper acetate added ; HQ = Hydroquinone added;

S = Small ; T = Trace ; Pyr. = Pyrolysand.

Table 13- Fractionation of liquid flow pyrolysates.

Run no.	Pyr.	Fract. 1	Fract. 2	Fract. 3	Fract. 4	Fract. 5	Fract. 6	Residue
1	IV (CA)	80-120 (S)	120-140 (6)					>140 (0.5)
2	IV (CA)	74-88 (S)	88-118 (S)	120-122 (S)	130-140 (25)			>140 (2)
3	IV (CA)	70-80 (S)	80-85 (S)	85-135 (S)	135-143 (50)			>143 (3)
4	IV (CA)	70-90 (S)	90-110 (S)	110-140 (23)				>140 (1)
5	IV (CA)	60-90 (1)	90 -100 (1)					>100 (26)
6	V (CA)	120-134 (0.5)	137-140 (8)					>140 (S)
7	VI	50-57 (4)						>57 (S)
8	VI			Not fractionated				
9	VII	76-85 (S)						>85 (S)
10	VIII (HQ)	148-170 (3)	170-176 (T)	178-190 (13)	88-94/ 12; (33)	136-140/ 12; (T)		>140/ 12; (16)
11	VIII (HQ)	145-156 (2.5)	165-175 (T)	175-187 (10)	88-92/ 12; (29)	ca. 120/ 12; (T)		>120/ 12; (22)
12	IX (HQ)	155-170 (3)	170-177 (T)	177-189 (7)	95-103/ 12; (21)	ca. 130/ 12; (T)		>130/ 12; (7)
13	IX (HQ)	159-169 (3.5)	169-174 (T)	176-187 (6)	94-104/ 12; (26)	ca. 130/ 12; (T)		>130/ 12; (6)
14	X	80-85/ 15; (T)	85-95/ 15; (39)					> 95/ 15; (T)
15	XI (HQ)	145-150 (73)						>150 (S)
16	XII (HQ)	160-165 (43)						>165 (S)

(contd.)

Abbreviations in Table 13.

CA - Copper acetate added ; HQ - Hydroquinone added;

S - Small ; T - Trace; Pyr. - Pyrolysand.

Table 13(Contd.)- Fractionation of liquid flow pyrolysates.

Run no.	Pyr.	Fract. 1	Fract. 2	Fract 3	Fract. 4	Fract. 5	Fract. 6	Residue
17	VIII (i)	140-150 (2)	87-94/ 12;(37)	ca.120/ 12;(T)				>120/ 12;(1)
18	VIII (ii)	140-148 (0.5)	155-174 (T)	176-186 (1.5)	88-94/ 12;(19)	120-130/ 12;(T)		>130/ 12;(4)
19	VIII (iii)	138-149 (0.5)	155-178 (T)	178-185 (1)	87-93/ 12;(9)	ca.120/ 12;(T)		>120/ 12;(3.5)
20	VIII (iv)	142-147 (2)	160-177 (T)	178-183 (4)	88-94/ 12;(7.5)	ca.120/ 12;(T)		>120/ 12;(8)
21	VIII (v) (HQ)	140-147 (1.5)	172-178 (T)	178-190 (4)	88-93/ 12;(5)	ca.120/ 12;(T)		>120/ 12;(10)
22	XIII (HQ)	90-100/ 3;(25)						>100/ 3;(T)
23	XIII (HQ)	114 (0.3)	114-120 (0.2)	120-150 (2.5)	25-65/ 1.5;(07)	65-70/ 1.5;(3.5)		> 70/ 1.5;(11)
24	XIII (HQ)	50-55 (1.5)	55-72 (1)	72-90 (1.5)	90-105 (0.5)	105-140 (2)		>140 (4)
25	XIII (HQ)	36-48 (1)	80-120 (0.5)	132-140 (2)				>140 (3)
26	XIV (HQ)	66-74 (1.5)	76-86 (1.5)	88-94 (1)	95-142 (2)			>142 (1)
27	XV	70-80 (0.5)	81-105 (0.5)	110-130 (0.5)	130-ca. 200(1.5)			>ca.200 (T)
28	XVI	95-108 (1.5)	110-130 (20)					>130 (8)
29	XVII	95-105 (2.5)						>105 (T)
30	XVII	95-105 (3.5)						>105 (T)

(contd.)

Abbreviations in Table 13.

CA - copper acetate added ; HQ - Hydroquinone added ;

S - Small ; T - Trace; Pyr. - Pyrolysand.

Table 13(Contd.)- Fractionation of liquid flow pyrolysates.

Run no.	Pyr.	Fract. 1	Fract. 2	Fract. 3	Fract. 4	Fract. 5	Fract. 6	Residue
31	XVIII (HQ)	65-85 (0.5)						>85 (S)
32	XVIII (HQ)	65-85 (8)						>85 (S)
33	XVIII (HQ)	65-75 (2.5)						>75 (22)
34	XIX	65-85 (1)	85-110 (9)	110-130 (1)				>130 (1)
35	XIX	75-83 (2)	90-110 (1)	110-130 (1.5)				>130 (10)
36	II			Not investigated.				
37	II	64-90 (0.5)	90-120 (3)	120-143 (0.2)	143-156 (0.5)	90-130/ 5; (1)	ca.140/ 5; (1)	>140/ 5; (11)
38	II	22-60 (3)	60-90 (0.5)	97-104 (1)	ca.80/ 5; (3.5)			>80/ 5; (17)
39	II	30-60 (0.6)	60-80 (0.3)	80-94 (0.3)	94-120 (0.5)	120-160 (0.4)	180-196 (0.1)	>196 (8.5)
40	II	20-60 (1)	60-90 (0.3)	90-110 (1)	110-145 (0.3)	152-190 (0.8)		>190 (22)
41	XX			Not investigated.				

Abbreviations in Table 14.

I.R. - Identification by infra-red spectrometry, comparison with standards except where wavelengths are quoted;

R - Residue ; P - Product in unfractionated pyrolysate ;

Pyr. - Pyrolysand.

Table 14- Analysis of liquid flow pyrolysates.

Pyr.	Product	Run	Fract.	Identification
IV	Acetaldehyde	1-5	1	2:4-DNP: m.156-60°, mixed m.160-62°; P.C.
	Acraldehyde	1-5	1	2:4-DNP: m.152-57°, mixed m.155-56°; P.C.
	Ethanol	2-5	1	I.R. After removal of aldehydes gives: (1) iodoform test, (2) Me.CHO (2:4-DNP, P.C.) from oxidation with $K_2Cr_2O_7$ - c.H_2SO_4, (3) pungent acid, resembling acetic, from oxidation with alkaline $KMnO_4$, (4) trace 3:5-dinitrobenzoate derivative.
	Water	1 2,4,5	1 2,3	Anhydrous $CuSO_4$; Fisher reagent
	Ethyl acrylate	1 2,4,5	1 2,3	I.R. n_D^{20} 1.402.
	Acrylic acid	1 2,3 4,5	2,R 4,R 3,R	I.R. -Dibromopropionic acid; m.119°, mixed m.119°. Acrylanilide; m.100°, mixed m.103°.
	Acetaldehyde	6	1	2:4-DNP: m.165°, mixed m.166°.
	Water	6	1	Anhydrous $CuSO_4$; Fisher reagent
	Acrylic acid	6	2,R	I.R. Acrylanilide; m.101°, mixed m.102°.

(contd.)

Abbreviations in Table 14.

I.R. - Identification by infra-red spectrometry, comparison with standards except where wavelengths are quoted ;

R - Residue ; P - Product in unfractionated pyrolysate ;

Pyr. - Pyrolysand .

Table 14(Contd.)- Analysis of liquid flow pyrolysates.

Pyr.	Product	Exp. no.	Fract. no.	Identification
VI	Acraldehyde	7 A	1 P	I.R. 2:4-DNP: m.161°, mixed m.161-68°.
VII	Acetaldehyde	9	1	2:4-DNP: m.163-64°, mixed m.165°.
	Ethanol	9	2,R	3:5-Dinitrobenzoate: m.92°, mixed 93°.
	Water	9	4,R	Anhydrous $CuSO_4$; Fisher reagent.
VIII	Styrene	10,11	1	1:2-Dibromoethylbenzene: m.72°, mixed m.73°.
	Phenyl formate	10,11	2	I.R. Green colour with ZnO_4. Formanilide: m.40-43°, mixed m.44-46°
	Phenol	10,11	3	m.40-41°, mixed m.41-42°. Phenyl benzoate: m.68°, mixed m.68°.
	Phenyl acrylate	10,11	4	I.R. n_D^{20} 1.522.
	β-Hydroxyacrylophenone (?)	10,11	5	I.R.; peak at 1740 cm.$^{-1}$(S) may derive from unsaturated ketone. Phenolic colour test. Decolorises Br_2/CCl_4. 2:4-DNP: m.239-40°. (Found: N,21.6. Calc. for $C_{15}H_{12}O_5N_4$: N, 17.1).

(contd.)

Abbreviations in Table 14.

I.R. - Identification by infra-red spectrometry, comparison with standards except where wavelengths are quoted ;

R - Residue ; P - Product in unfractionated pyrolysate ;

Pyr. - Pyrolysed.

Table 14(Contd.)- Analysis of liquid flow pyrolysates.

Pyr.	Product	Run No.	Fract.No.	Identification
IX	α-Methylstyrene	12,13	1	I.R. n_D^{20} 1.536. 1':2'-Dibromo-1'-methylbenzene: b.115-125°/8 mm. (Lit., Grignard[104], b.115°/8 mm). Oxidation with cold $KMnO_4$ yields No.60.Ph (2:4-DNP: m.246°, mixed m.247°).
	Phenyl formate	12,13	2	I.R. Green colour with $KMnO_4$. Formanilide: m.38-41°, mixed m.41-43°.
	Phenol	12,13	3	m.42°, mixed m.42°. Phenyl benzoate: m.68°, mixed m.68°.
	Phenyl α-methyl-acrylate	12,13	4	I.R. n_D^{20} 1.515.
	p-Hydroxy-α-methylstyryl-methylstyryl-phenone(?)	12,13	5	I.R.; peak at 1720 cm.$^{-1}$(S) may derive from unsaturated ketone. Phenolic colour test. Decolorises Br_2/CCl_4. 2:4-DNP: m.254°. (Found: C,54.0; H,3.6; Calc. for $C_{25}H_{14}O_5N_4$: C, 56.1; H, 4.1).
X	Phenyl formate	14	1	I.R. Formanilide: m.42-43°, mixed m.44°.
	Phenol	14	2,3	m.40°, mixed 41°. Phenyl benzoate: m.69°, mixed m.69°.
XI	Styrene	15	1	I.R. n_D^{20} 1.547.
III	α-Methylstyrene	16	1	I.R. $n_{D?}^{20}$ 1.538.

(contd.)

Abbreviations in Table 14.

I.R. - Identification by infra-red spectrometry, comparison with standards except where wavelengths are quoted ;

R - Residue ; P - Product in unfractionated pyrolysate ;

Pyr. - Pyrolysand .

Table 14(Contd.)- Analysis of liquid flow pyrolysates.

Pyr.	Product	Run No.	Fract.No.	Identification
XIII	Acetaldehyde	23-25	1	2:4-DNP: m.152-54°, mixed m.152-56°. P.C.
	Acraldehyde	24	1	2:4-DNP: m.156-57°, mixed m.157-59°. P.C.
	Hexa-1:5-diene	24	1,2	I.R.
	Methyl vinyl ketone	24	1,2	I.R.
		25	2	2:4-DNP (crude trace).
	Methyl acrylate	24	3	I.R.
		25	3	
	Vinyl acrylate	24	4	I.R. Hydrolysis with 50% KOH yields
		25	3	CH_2:CH.COOH (acrylanilide: m.98-100°, mixed m.100-102°) and Me.CHO (2:4-DNP: m.153-55°, mixed m.155°) P.C.)
	Water	23	1	Anhydrous $CuSO_4$; Fisher reagent.
		24	4	
		25	3	
	Acrylic acid	23,25	3	I.R. Acrylanilide: m.99-101°, mixed m.102-105°
		24	5	
	Ethylene diacrylate	22-25	R	I.R.

(contd.)

Abbreviations in Table 14.

I.R. - Identification by infra-red spectrometry, comparison with standards except where wavelengths are quoted ;

R - Residue ; P - Product in unfractionated pyrolysate ;

Pyr. - Pyrolysand .

Table 14(Contd.)- Analysis of liquid flow pyrolysates.

Pyr.	Product	Run No.	Fract. No.	Identification
XIV	Acetaldehyde	26	1	2:4-DNP: m.152-60°, mixed m.161-62°.
	Methyl vinyl ketone	26	1,2	I.R.
	Vinyl acrylate	26	2,3	I.R. Bayer colour test.
	Water	26	R	Anhydrous $CuSO_4$; Fisher reagent.
	Acrylic acid	26	R	I.R. Acrylanilide: m.103°, mixed m.103°.
	Acryloylacetaldehyde(?)	26	R	2:4-DNP: m.172-74°. (Found: C,48.4; H,3.8. Calc. for $C_9H_6O_2$: C,44.5; H,3.3).
XV	See p. 133			
XVI	Crotonaldehyde	28	1	2:4-DNP: m.166°, mixed m.169°.
	Methyl crotonate	28	R	I.R.
XVII	Crotonaldehyde	29,30	1	I.R. 2:4-DNP: m.169°, mixed m.169°.
XVIII	Formaldehyde	31-33	1	2:4-DNP: m.164-65°, mixed m.165°. P.C. (Extracted by MeOH from a mixture with CH_2:CH.CHO + 2-4 DNP).
	Acraldehyde	31-33	1	2:4-DNP: m.162°, mixed m.164°.
	Methanol	33	1	I.R.

(contd.)

Abbreviations in Table 14.

I.R. = Identification by infra-red spectrometry, comparison with standards except where wavelengths are quoted ;

R = Residue ; P = Product in unfractionated pyrolysate ;

Pyr. = Pyrolysate .

Table 14(Contd.)- Analysis of liquid flow pyrolysates.

Pyr.	Product	Run No.	Fract.No.	Identification
XVIII (Contd.)	Methyl acrylate	31,32	1	I.R. n_D^{20} 1.399
		33	R	
	Water	33	R	Anhydrous $CuSO_4$; Fisher reagent.
XV (XIX)	Formaldehyde	27 (34,35)	1	2:4-DNP: m.164°, mixed m.165°; P.C.
			1	(Extracted by MeOH from a mixture with CH_2:CH.CHO 2:4-DNP).
	Acraldehyde	27 (34,35)	1	2:4-DNP: m.158-59°, mixed m.159-60°; P.C.
			1	
	Methanol	27 (34,35)	1	I.R.
			1	
	Methyl acrylate	27 (34,35)	2	I.R. n_D^{20} 1.3984.
			2	
	Water	27 (34,35)	2	Anhydrous $CuSO_4$; Fisher reagent.
			2	
	Crotonaldehyde	27 (34,35)	2	I.R. 2:4-DNP: m.165-65°, mixed m.169°; P.C.
			2	
	Methyl crotonate	27 (34,35)	3	I.R.
			3	
XIX	Methyl malonate	34,35	R	I.R. n_D^{20} 1.4416.

(contd.)

Abbreviations in Table 14.

I.R. - Identification by infra-red spectrometry, comparison with standards except where wavelengths are quoted ;

R - Residue ; P - Product in unfractionated pyrolysate ;

Pyr. - Pyrolysand .

Table 14(Contd.)- Analysis of liquid flow pyrolysates.

Pyr.	Product	Run No.	Pract.No.	Identification
II	Acetaldehyde	37-40	1	2:4-DNP: m.157-58°, mixed m.158°; P.C.
	Vinyl acrylate	37	2	I.R. Ester colour test.
		38-40	3	After removal of Mg.OHO yields on hydrolysis with 50% EOH Mg.OHO (2:4-DNP; m.158-54°, mixed m.154-55°).
	Water	37	2	Anhydrous $CaSO_4$; Fisher reagent.
		38,40	3	
		39	4	
	Acrylic acid	37	3	I.R. Acrylonilide: m.97-98°, mixed m.99°.
		38,40	4	
		39	5	
	Non-fumarate polyester	37-40	R	I.R.; Characteristic fumarate peak at 975 cm.$^{-1}$ absent, spectrum altered in region of the carbonyl frequency.
				Hydrolysis with 50% EOH yields only liquid acids, no fumaric acid.
				Thermoplastic; soluble in organic solvents.
XI	Acrylic acid	41	P	I.R.

Abbreviation in Table 15.

I.R. - Identification by infra-red spectrometry, comparison with standards except where wavelengths are quoted.

Table 15- Extraction of liquid flow pyrolysates.

Pyr.	Product	Run No.	Extract	Identification
VI	Low mol.wt.non-acid materials	37	Et_2O	Trace only, not characterised.
	Acrylic acid	39,40	5% aq. NaOH	I.R.
	Fumaric acid	37-39	5% aq. NaOH	I.R. m.280-85°, mixed m.283-85° (subliming, sealed tube).
	Poly(ethylene fumarate), DP_n 2.5	37	$CHCl_3$	I.R. N(oxy. in benzene) 380, determined after removal of acids with 5% aq. NaOH and other low mol.wt. products with Et_2O.
	High mol.wt. carboxylic acids	37-39	5% aq. NaOH	I.R.; strong absorption peaks at ca 1710 $cm.^{-1}$. Thermoplastic; soluble in polar organic solvents.
	Non-fumarate linear polyester	38-39	$CHCl_3$	I.R.; characteristic fumarate peak at 975 $cm.^{-1}$ absent, spectrum altered in region of the carbonyl frequency. Thermoplastic; soluble in organic solvents.

Abbreviations in Table 16.

5 - Product collected with liquid pyrolysate fraction 5 ;

R - Product detected in liquid pyrolysate distillation residue ;

F - Product filtered from liquid pyrolysate before distillation ;

I.R. - Identification by infra-red spectrometry, comparison with standards.

Table 16- Analysis of solid pyrolysates

Pyr.	Product	Run No.	Fract. No.	Identification
VIII	Naphthalene	10,11	5	m.79°, mixed m.60°(subliming, sealed tube). I.R. Green colour with $AlCl_3$, $CHCl_3$.
	Poly(phenyl acrylate)	10,11	R	I.R.
IX	2:3-Dimethylnaphthalene	12,13	5	m.100°, mixed m.100°(subliming, sealed tub I.R. Green colour with $c.H_2SO_4$. Found: C,92.6; H,7.5; M(cryo. in benzene) 150. Calc.for $C_{12}H_{12}$: C,92.3; H,7.7; M,15
	Poly(phenyl α-methyl-acrylate	12,13	R	I.R.
XI	Polystyrene	15	R	I.R.
XII	Poly-α-methylstyrene	16	R	I.R.
XIII	Compound	24,25	F	Trace only, not characterised.
XV (XIX)	Triozane	27 (34,35)	F F	m.58-60°, mixed m.60-61°.
	Methyl fumarate	27 (34,35)	F F	m.102°, mixed m.102°.
XVIII	Trioxane	33	F	m.60°, mixed m.61°.
XX	Formic acid	41	F	m.286°, mixed m.286°(subliming, sealed tube

Abbreviation and symbol in Table 18.

* - DP_n value the average of three determinations by end-group analysis ;

I - Pyrolysate insoluble.

Table 17- Analysis of flow pyrolysis 2:4-DNP trap derivatives.

Pyr.	Product	Run no.	Identification
IV	Acetaldehyde	1	m.162-64°, mixed m.164-65°.
XIII	Acetaldehyde	22-25	m.167°, mixed m.168°.
XIV	Acetaldehyde	26	m.162-63°, mixed m.164-66°.
XV (XIX)	Formaldehyde	27 (34,35)	m.163-64°, mixed m.164-66°.
II	Acetaldehyde	36-40	m.168°, mixed m.168°.

Table 18- Static pyrolysis of II, DP_n initially 5.4 .

Run no.	42	43	44	45
Temperature, °C.	250	250	250	300
Reactor type	5	5	5	5
Contact time, mins.	30	60	75	10
DP_n value*	16.3	48.4	I	I

Table 19- Comparison of gas evolution from II, XXI and XXII.

Run no.	46	47	48
Pyrolysand	II	XXI	XXII
Reactor type	4	4	4
Pyrolysand wt., g.	9.7	9.9	9.5
Contact time, mins.	15	15	15
Gaseous pyrolysate vol.,l. at N.T.P.	520	340	280
% Composition of gaseous pyrolysate:			
Carbon dioxide	32	30	39
Unsaturated gases	16	20	4
Carbon monoxide	52	50	57
Gas evolution in ml./g. pyrolysand	55	34	30

Abbreviation and symbol in Table 20.

- - Nil ; MF - Methyl fumarate;

Table 20- Comparison of methyl α-methylacrylate liberation from Ia, III, XXIII and XXIVa.

Run no.	49	50	51	52	53	54	55	56
Pyrolysand	Ia	III	XXIII	XXIVa	Ia	III	XXIII	XXIVa
Temperature	200	200	200	200	250	250	250	250
Reactor type	5	5	5	5	5	5	5	5
Pyrolysand wt., g.	1.39	1.0	1.30	1.39	1.39	1.0	1.30	1.39
Contact time, mins.	60	60	60	60	120	120	120	120
Methyl α-methylacrylate evolution, g.	T	0.06	0.04	0.03	0.11	0.28	0.20	0.15
%	T	6	4	3	11	28	20	15
Other products	H_2O	-	MF	H_2O	H_2O	-	MF	H_2O

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